79

PhilipMorris

RESEARCH CENTER

TECHNICAL REPORT NO. 203

LOW COST BL BINDER FORMULATION -
USE OF BENTONITE

0000331014

TECHNICAL REPORT

Document hosted at http://www.industrydocuments.ucsf.edu/docs/yfkx0000

For Reference
Not to be taken from this room

ϕ000331015

79

Copy No. 1

PHILIP MORRIS INC.

RESEARCH CENTER

Richmond, Virginia

December 31, 1960

TECHNICAL REPORT NO. 203

LOW COST BL BINDER FORMULATION - USE OF BENTONITE

Prepared by

H B Merritt

H. B. Merritt

Approved by

J D Hind

J. D. Hind

Distribution

Mr. W.H. Hatcher
Mr. R.P. Roper
Mr. R.R. Millhiser
Mr. C.H. Goldsmith
Mr. H. Cullman
Mr. A.C. Britton
Mr. G.W. Macon,Jr.
Mr. J.E. Lincoln
Mr. W.F. Sperber
Dr. H. Wakeham
Mr. C.B. Guthrie,Jr.
Mr. W.R. Wilkinson
Dr. R.B. Seligman

ϕ0003310 16

M. F.

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table of Contents

I. Introduction and Summary 1

II. Conclusions 2

A. Toxicity of Bentonite 2

B. BL Pilot Plant Manufacture and Evaluation . . 3

1. Processability 3

2. Sheet Properties 3

3. Cigarette Evaluation 3

a. Coal Strength 3
b. TPM and Nicotine in the Smoke 3
c. Non-tobacco Combustibles 3
d. Taste Panels 3

C. Patents and Licensing 4

D. Economics 4

III. Discussions, Results, and Procedures 4

A. Description of Bentonite 4

B. Toxicity of Bentonite 5

1. Inorganics in the Smoke 5

2. Literature Search 5

3. Contacts with Outside Toxicologists and Toxicology Laboratories 5

C. BL Pilot Plant Manufacture and Evaluation. . . 5

1. Pilot Plant Experiments 5

2. Cigarette Evaluations 7

a. Coal Strength 7
b. TPM and Nicotine in the Smoke 7
c. Taste Panel 8

D. Patents and Licensing. 8

C. Cost Analysis 8

Φ000331017

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table of contents (continued)

IV. Recommendations 9

A. In the Production Plant 9

B. In the Cigarette Manufacturing Operation 9

C. In the Pilot Plant 9

D. In the Laboratory 10

Tables

I. Binder Formulations Compared During This Study (in text, see page 2)

II. Whittaker, Clarke & Daniels, Inc. #49 Bentonite

III. Sheet Physical Properties Comparison (Bentonite Binder vs. Old Standard Production Binder Using High Viscosity CMC)

IV. Sheet Physical Properties Comparison (Bentonite Binder vs. New Standard Production Binder Using Medium Viscosity CMC)

V. Coal Strength Comparison Test Summary (R & D Coal Strength Tests)

VI. Comparison of TPM and Nicotine Delivery

VII. Percent Composition of BL Sheet

VIII. Taste Panel Evaluation

IX. Annual Binder Cost Calculations

X. Annual Binder Cost Comparison

Exhibits

1. "The Scientific Aspects of Bentonite" published by the American Colloid Company

2. Memo from J. C. Holmes to L. S. Harrow, August 10, 1960 entitled "Amount of Bentonite in Smoke", and memo from Virginia Johnson to J. C. Holmes, July 21, 1960 entitled "Deposits from Cigarette Smoke"

3. "Biology of Bentonite" by S. Solomon, September 7, 1960, memo L. S. Harrow to H. Merrit, June 15, 1960 entitled "Proposed Coroborative Proof of Innocuousness of Bentonite", and memo L. S. Harrow to Henry Merritt, July 12, 1960 entitled "Bentonite"

bl00331018

Source: https://www.industrydocuments.ucsf.edu/docs/kmnd0000

Table of Contents (continued)

4a. Letter from Kenneth Morgareidge, Food and Drug Research Laboratories, Inc. to J. C. Holmes, March 16, 1960 regarding ". . . possible significance to the smoker of minute traces of Bentonite inhaled with the smoke of cigarettes made from "BL" containing the mineral."

4b. Letter from S. R. Mountsier, Jr., Whittaker, Clarke & Daniels, Inc. to Henry B. Merritt, May 26, 1960, ". . . under the Food Additive Amendment to the Food and Drug Law, that Bentonite was listed as a material which was generally regarded as safe and not limited in any way."

5. Memo R. B. Seligman to H. B. Merritt, August 4, 1960 entitled "Coal Strength Measurement of 100% BL Cigarettes (Bentonite Binder)"

6. Memo C. E. Maxwell, Jr. to H. B. Merritt, September 12, 1960 entitled "Panel Tests Showing the Effect of Bentonite on Smoke Flavor (All cigarettes Chico-Made Unless Noted)"

7 Letter from E. R. Helferich to Henry B. Merritt, August 12, 1960 re: "Use of Bentonite in BL, Our File 582-152"

Φ0003310 19

Source: https://www.industrydocuments.ucsf.edu/docs/[illegible]

I. Introduction and Summary

During the investigation conducted on the low tar filler program, it was observed that various types of bentonite (an inorganic, clay-like material) had film-forming and binding properties similar to those of the organic gums currently in use in the BL binder. Discussions of these observations with various persons in the Research Center indicated the following areas of interest as to the usefulness of bentonite in the BL binder film:

1. The use of bentonite in the binder might result in a cost savings because bentonite, at $0.026/pound, would replace CMC, at $0.62/pound.

2. Substitution of the inorganic, non-combustible bentonite for a portion of the combustible CMC might improve the smoke flavor of the finished sheet because the total quantity of non-tobacco combustibles would be reduced.

3. Use of bentonite might improve the sheet's properties, in particular the coal strength of the BL in the filler blend. Bentonite, an inorganic film-former which is not destroyed by burning, might effect a fortification of the ash and the burning coal.

Thus, further investigations were undertaken to evaluate the possible advantages of incorporating bentonite into the BL binder.

A satisfactory bentonite formulation for initial pilot plant work was developed in the laboratory, and pilot plant experiments and subsequent product evaluations were made. Based on the work in both the laboratory and the pilot plant there is sufficient evidence presently on hand to warrant the use of bentonite in the BL binder without further delay. In the remainder of this report it will be shown:

1. That a savings of approximately $240,000/year can be realized immediately.

2. That a significant improvement in the coal strength of 100% BL cigarettes can be made without altering any other of the sheet's physical properties or modifying any of the present production equipment.

During this investigation the standard binder formulation and binder weight were changed in the BL production process. A comparison was thus made testing the bentonite formulation against both the old and the new standard production formulations. The bentonite formulation used in this investigation is shown in the following table: (In the remainder of this report any reference to a bentonite

0000331020

Source: https://www.industrydocuments.ucsf.edu/docs/xxxxxxx

formulation or bentonite binder will be to the formula as listed in the following table.)

Table I

Binder Formulations Compared During This Study

	Old Production Standard, 1.2 gm/ft²		Suggested Bentonite, 1.6 gm/ft²		New Production Standard 1.6 gm/ft²	
	Parts	%	Parts	%	Parts	%
Tobacco pulp	1.0	37.8	1.0	42.6	1.5	47.65
Bentonite	---	----	0.5**	21.3**	---	----
CMC	1.0 (7H)	37.8	0.5*	21.3*	1.0 (7M)	31.75
Propylene glycol	0.5	18.9	0.25	10.8	0.5	15.85
Acid	0.15 (pH 2.7)	5.65	0.10 (pH 4.0)	4.2	0.15 (pH 2.7)	4.75

* Investigations using both high (7H) and medium (7M) viscosity CMC were made. The use of 7M in the bentonite formulation is recommended for production at the higher binder weight (1.6 gm/ft²).

** The mixing procedure used to prepare the bentonite binder is similar to that used to prepare the new standard production binder. The only change required is the addition of the bentonite after the addition of the pulp. Experiments indicate pHs in the range of 2.6-5.0 are satisfactory.

II. Conclusions

The conclusions presented here are based on information and data collected during laboratory investigations and on material produced in eleven pilot plant experiments.

A. Toxicity of Bentonite

Based on work done by our Analytical Division on an extensive literature search, and on statements from outside toxicology experts, it is reasonable to state that there will be no toxic reaction on the smoker due to the incorporation of bentonite in the BL binder.

00031021

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

B. BL Manufacture and Evaluation

1. Processability

Discussions with Manufacturing Department personnel regarding the processability of a special pilot plant BL made with a bentonite binder indicated that its processability on the present blending, cutting and making equipment was equal to that obtainable with standard production BL.

2. Sheet Physical Properties

At similar binder weights the physical properties of BL sheets based on the bentonite binder are equivalent to the physical properties of BL sheets based on either the old or the new standard production binders.

3. Cigarette Evaluation

a. Coal Strength

At the same binder weights, cigarettes made from 100% BL based on bentonite binder are significantly stronger in coal strength (Research Center tests) than those prepared with either the old or the new standard production formulations.

b. TPM and Nicotine in the Smoke

No change in the delivery of TPM or nicotine occurred either in 100% BL cigarettes or in cigarettes made from an 80% Parliament, 20% BL blend due to the incorporation of bentonite in the BL binder film.

c. Non-tobacco Combustibles

The use of bentonite binder results in a reduction in the non-tobacco combustibles in the BL binder of between 40-52% (7.5% of the total sheet reduced to 3.5% of total sheet).

d. Taste Panel

No difference in smoke taste or preference was found when comparing cigarettes containing bentonite BL against cigarettes containing old or new standard production BL (100% BL cigarettes and 80% Parliament, 20% BL blends.)

ϕ0003310 22

Source: https://www.industrydocuments.ucsf.edu/docs/xkmx0000

C. Patents and Licensing

The use of bentonite in the binder formulation will not alter our present position with regard to existing patents or licensing agreements.

D. Cost Analysis

An annual savings of approximately $240,000/year can be made by substituting the bentonite formulation for the new standard production BL binder formulation (based on annual usage of CMC of 1,092,000 lb/year).

III. Discussion, Results, and Procedures

A. Description of Bentonite (also see Exhibit 1, Appendix B)

Bentonite, an inorganic clay-like material, is derived from volcanic ash. It is an extremely variable material in both its outward appearance and superficial physical properties; the variations result from the different crystalline structures which the material inherited from its origin.

During the investigation of several inorganic materials for use in the LTF* program it was observed that some types of bentonite exhibited film forming properties similar to those attributed to the organic gums used in the BL binder. Further studies of the different types of bentonites revealed that those which swelled greatly in water to form plastic-like inorganic mixtures exhibited the greatest promise as film-forming materials.

The swelling and the film-forming abilities are primarily due to the micaceous habit of the material and to the very slight cohesion between the crystalline plates. On wetting, water penetrates between the crystalline plates shattering the aggregate, thereby producing a large number of colloidal particles that have a large lateral extent and a thickness in molecular dimensions. Each of these colloidal, crystalline plates is surrounded by an envelope of water molecules. This associated water causes apparent swelling of the bentonite particles which produces a thixotropic, plastic-like mixture. The film-forming properties exhibited by these swelling types of bentonite results from the orderly overlapping of and re-development of cohesive forces between the crystalline plates as water is removed by evaporation.

The type of bentonite selected for further investigation was the highly swelling Wyoming-type of bentonite (#49) supplied by Whittaker, Clarke, & Daniels. The chemical and physical analysis of this material as reported by Whittaker, Clarke, & Daniels is shown in Table II, Appendix A.

ϕ00331023

* Low Tar Filler (Research Center Project #1500)

Source: https://www.industrydocuments.ucsf.edu/docs/ϕϕϕϕϕϕϕϕ

B. Toxicity of Bentonite

1. Inorganics in the Smoke

In order to evaluate the possible toxic effects on the smoker of inhaling smoke from cigarettes made from bentonite-containing BL, it was first necessary to determine the amount of bentonite in that smoke. This was done by conventionally determining the amount of inorganic ash in the smoke from unfiltered, 100% BL cigarettes made from both bentonite-containing BL and from non-bentonite containing BL. The results are discussed in a report form the Special Investigations Section (Exhibit 2, Appendix B). These tests show that there is no increase in the amount of inorganic ash in the smoke of 100% BL cigarettes when as much as 3.4% bentonite is present in the BL. (The recommended formula contains 3.4% bentonite in the BL sheet.) In fact, it appears that the addition of bentonite to the BL may even reduce the total quantity of inorganic ash in the smoke. The reduction may result from the ash fortification by the non-combustible film-forming bentonite; that is, less ash breaks off and, thus, less ash is carried to the smoker in the smoke stream. Ash determinations were also made on standard Parliament cigarettes (containing bentonite BL) made up by the Manufacturing Department and on Marlboro monitor cigarettes. These tests lead to conclusions identical to those obtained on 100% BL cigarettes.

2. Literature Search

Extensive literature searches were made to obtain background information concerning the possible toxicity of bentonite. Many reports were found describing the use of bentonite in drug and cosmetic formulations, in dietary supplements for livestock, and in other FDA-approved items. No reports were found which indicated that a toxic reaction might result from smoking 100% BL cigarettes containing bentonite in the binder (see Exhibit 3, Appendix B).

3. Contact with Outside Toxicologist and Toxicology Laboratories

In an effort to further improve and update our understanding of the toxic effects of bentonite in cigarette smoke, contacts were made with outside laboratories and with persons who were believed to be expert in the toxicology field. These authorities again confirmed the hypothesis that no toxic effects to the smoker would result from the use of bentonite in the BL binder (Exhibits 4a&b, Appendix B).

C. BL Manufacture and Evaluation

1. Pilot Plant Experiments

The laboratory investigations indicated that a usable binder film could be made with as much as 65-70% of the CMC

0000331024

Source: https://www.industrydocuments.ucsf.edu/docs/xxxx0000

in the present formulation replaced by bentonite. The major efforts in the laboratory were aimed at the development of a satisfactory bentonite formulation for use in pilot plant experiments. It should be realized that it was impossible to obtain the optimum binder formulation in the laboratory, due to the difficulty of bridging the gap from laboratory prepared binder films to finished BL sheet as produced in the plant. The final "optimization" will best be accomplished in the pilot plant. The formulation selected for the pilot plant investigations was the old standard production formulation with a 50% substitution of the CMC by bentonite, accompanied by a 50% reduction in the propylene glycol (see Table I).

Six experimental trials were made in the pilot plant comparing the old standard formulation with the bentonite formulation. Both binder slurries were made up using high viscosity CMC (7H). (See Table III in Appendix A for a comparison of the sheet properties obtained from materials produced during these trials.) A study of the physical properties of the materials produced showed that at equal binder weights the material based on the bentonite binder was equivalent to the material based on the old standard production binder. As observed in previous experiments using the old standard binder, the physical properties of the sheet based on the bentonite binder improved as the binder weight increased.

While these comparative experiments were being made, the standard formulation used in the BL production plant was changed and the standard binder weight was increased from 1.2 to 1.6 grams/sq. ft. In order to increase the binder weight and still maintain the same production speeds it was necessary to increase the percentage solids in the binder slurry. This was accomplished without a substantial increase in the slurry viscosity by changing from high viscosity CMC to medium viscosity CMC. A comparison of the bentonite formulation and the new standard production formulation is shown in Table I.

Four experimental trials were made in the pilot plant comparing the new standard production formulation with the bentonite formulation using medium viscosity CMC. A comparison of the sheet properties obtained from material produced during these trials is presented in Table IV, Appendix A. A study of the data shows that equivalent sheet properties were obtained when equal binder weights were used.

In summation it can be said that sheet properties equivalent to those obtained using the old standard or the new standard binder formulation were obtained with the bentonite formulation when equal binder weights were used. It also follows that a replacement with bentonite of at least 50% of the CMC used in the binder formulation can be made without degrading the sheet's properties. In fact, as will be shown in the section entitled "Coal Strength", an improvement in the BL sheet's properties can be obtained.

Φ00031025

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

2. Cigarette Evaluation

To further evaluate the BL produced in the pilot plant cigarettes were manufactured on the Chico machine at the Research Center and on production equipment by the Manufacturing Department. The following evaluations were made.

a. Coal Strength (See Exhibit 5, Appendix B)

The relative effect on the coal strength (Research Center tests) of the incorporation of bentonite in the BL binder was determined by comparing the coal strength of sets of cigarettes which were manufactured in a duplicate manner on the Chico maker (bentonite binder vs. old or new binder BL). The results of these investigations are reported in Table V, Appendix A. A study of the results indicates the following:

1. At the same binder weight, BL made from the bentonite-type binder is significantly stronger in coal strength than those prepared with either the old or new standard production formulations (1.6 gm/ft^2 bentonite vs. 1.6 gm/ft^2 new standard, 1.2 gm/ft^2 bentonite vs. old standard).

2. There is no significant difference in the coal strength of 100% BL cigarettes made from BL based on the bentonite-type binder at 1.2 gm/ft^2 and BL based on the new standard binder at 1.6 gm/ft^2 (both using 7 medium CMC).

The conclusions stated above are based on tests conducted with 100% BL cigarettes and are thus only an indication of the effect that might be expected in cigarettes containing BL at the current levels in use in the Manufacturing Department (21% BL or less). Attempts have been made to measure the change in coal strength of Parliament blends. However due to the dilution of the BL (21% or less in Parliament blend) and the poor precision of the test, no significant difference has been shown (Research Center test).

b. TPM and Nicotine in the Smoke

The TPM and nicotine delivered in the smoke of 100% BL cigarettes and standard Parliament cigarettes made from both bentonite BL and from old and new standard BL was determined. The data are reported in Table VI, Appendix A. A study of the data indicate that no change in the delivery of TPM or

bg0031026

Source: https://www.industrydocuments.ucsf.edu/docs/XMW0050

nicotine occurred in either the 100% BL cigarettes or the standard Parliament BL blends due to the inclusion of bentonite in the BL binder. This result was expected because bentonite is an inactive, inorganic material and is present in relatively low percentages; 3.4% or less of the finished BL sheet.

c. Taste Panel (Exhibit 6, Appendix B)

Taste panels were run to determine if the use of bentonite in the BL binder altered the taste of the smoke. Consideration of the amount of bentonite in the sheet, 3.4% or less, and the fact that it is inorganic leads one to expect little or no effect on the smoke. However, when one considers the fact that there is a reduction in the non-tobacco combustibles of about 45%, (see Table VII), a change in the smoke flavor might be expected. The results of taste panels comparing cigarettes containing bentonite BL against cigarettes containing standard BL at various levels (100% BL cigarettes, 20% BL and 80% BL-free Parliament cigarettes, and standard production-made Parliament cigarettes) are reported in Table VIII. A study of these test results indicate that there is no difference or preference (bentonite BL vs. standard BL) in the smoke taste of 100% BL cigarettes, and that when the BL is diluted with filler to levels similar to those currently in use, there is, again, no difference in taste or preference (bentonite BL vs. standard BL).

D. Patents

The use of bentonite in the binder formulation will not alter our present position with regard to existing patents or licencing agreements (Exhibit 7, Appendix B).

E. Cost Analysis

The investigations conducted to date on the use of bentonite in the BL binder indicate that bentonite can be used to replace 50% of the CMC in the BL sheet with no change in the physical properties of the sheet. An economic analysis was conducted to determine the monetary effects of such a change. The calculations noted in Table IX and compared in Table X were based on the current annual rate of consumption of CMC of 1,092,000 lb/year (equivalent to an annual usage of binder of 3,448,000 lb/year).

0003102

Source: https://www.industrydocuments.ucsf.edu/docs/

These calculations indicate that an annual savings of $240,000 can be made by substituting the recommended bentonite formulation for the new standard formulation now in use. (Both calculations are based on binder weights of 1.6 gm/ft².)

While the recommended bentonite formula was being evaluated in the pilot plant, efforts were continued in the laboratory to further optimize a bentonite formulation. Although these formulas currently under laboratory investigation have not been evaluated in the pilot plant, it appears reasonable to expect that additional savings may be realized. Because of this, calculations have been included in Table IX and Table X comparing the new standard binder formulation with the recommended bentonite formulation and with an optimized bentonite formulation. Calculations using the optimized bentonite formula (based on a 1.2 gm/ft² binder weight) indicate that an additional saving of approximately $200.000 may be realized over and above the $240,000 saving which can be accomplished by adoption of the recommended bentonite formula. To put it another way, successful adoption of an optimized bentonite binder formula has the potential of saving $440,000 annually in binder costs at our present rate of BL production.

IV. Recommendations

A. In the BL Production Plant

Efforts should be made to incorporate the bentonite binder into the BL production process. The binder slurry should be prepared at 4.7%-5.0% solids using 7 medium CMC, and BL sheet produced using a binder weight of 1.6 gm/ft².

B. In the Cigarette Manufacturing Operation

Final evaluation of any BL process or formula change must be made during filler processing and subsequent cigarette manufacture, It is recommended, therefore, that this new-formula production BL be closely monitored during several trials of filler processing and cigarette manufacture.

C. In the BL Pilot Plant

1. Continue the present program aimed at optimizing the bentonite formulation.

2. Continue the program to evaluate the usefulness of the bentonite in the belt water and the humidification water.

2000331028

Source: https://www.industrydocuments.ucsf.edu/docs/jpm00000

D. In the Laboratory

Continue the present program aimed at increasing our understanding of the contribution of the various binder ingredients to the properties of bentonite-type binders. That is:

percentage and type of gum (film-former)
percentage and type of plasticizer
percentage and type of pulp
percentage and type of bentonite

/hj

ϕ00331029

Source: https://www.industrydocuments.ucsf.edu/docs/kjnf0000

0000331030

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table II

Whittaker, Clarke & Daniels, Inc.

#49 Bentonite

Use:

Foundries, asphalt emulsions, polishes, paper

Average Dry Sieve Analysis	
Thru 200 mesh	85-90%
Wet Sieve Analysis (Dispersed in Water)	
Finer than 200 mesh	96%
Finer than 20 microns	93%
Finer than 0.5 micron	86%

Typical Chemical Analysis

SiO_2	64.32%
Al_2O_3	20.74
Fe_2O_3	3.03
FeO	0.46
TiO_2	0.14
P_2O_5	0.01
CaO	0.52
MgO	2.30
Na_2O	2.59
K_2O	0.39
SO_3	0.35
H_2O	5.14

Type of bentonite used in primary pilot plant runs.

00031031

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table III

Sheet Physical Properties Comparison

Bentonite Binder vs Old Standard Production Binder Using High Viscosity CMC (See Table I)

At equal binder weights the material based on the bentonite binder was equivalent to the material based on the old standard binder (216A vs 216B; 230A vs 228 control).

Pilot Plant Experiment No.	216**			230		
	A*	B	C	A	B	228*
Binder type	Old std.	Bent.	Bent.	Bent.	Bent.	Old std.
Binder weight, gm/ft²	1.2	1.2	2.4	1.2	1.6	1.2
Basis weight	8.8	8.7	10.4	8.2	9.2	9.5
Moisture, %	12.0	11.3	12.0	12.6	11.0	12.1
Tensile, Kg/in.	0.84	0.87	1.2	0.91	0.96	0.85
Tear, gm	5.3	4.9	12.8	4.3	6.4	6.1
Dust loss, GPF	1.1	1.4	1.3	0.78	0.87	0.68
Dust off, cpf	6.1	0.8	9.95	0.45	0.51	0.23
Breakage, %	62.4	72.0	54.5	28.7	29.7	26.0
Filling power, cc/10 gm	42.0	31.0	46.0	42.0	46.0	41.0
Burning rate, mg/sec.	1.8	1.8	1.8	1.6	1.5	1.5

* Control

** Sheet was also made using bentonite binder at 0.8 gm/ft². Tensile for this material was 0.7 Kg/in.

2801330000

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table IV

Sheet Physical Properties Comparison

Bentonite Binder vs. New Standard Production Binder Using Medium Viscosity CMC (See Table I)

At equal binder weights the material based on the bentonite binder was equivalent to the material based on the new standard binder (273A vs. 273B).

Pilot Plant Experiment Number	245-248		273	
	A	B*	B	A*
Binder type	Bent.	New std.	Bent.	New std.
Binder weight, gm/ft^2	1.2	1.6	1.6	1.6
Basis weight	8.7	9.6	9.6	10.1
Moisture, %	11.7	12.4	12.2	12.4
Tensile, Kg/in.	0.8	1.0	1.10	1.05
Folded tensile, Kg/in.	0.68	0.96	1.03	1.07
Tear, gm	5.4	8.1	6.5	6.6
Dust loss, GPF	0.85	0.61	0.68	0.58
Dust off, GPF	0.50	0.36	0.48	0.38
Breakage, %	18.1	14.9	11.32	2.57
Filling power, cc/10 gm	38	39	40	38
Burning rate, mg/sec.	1.6	1.5	1.6	1.8
Burning rate, %	94.4	86.8	94.7	94.8

* Control

00033103

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table V

Coal Strength Comparison Test Summary
(R & D Coal Strength Tests)

Cigarettes made on Chico maker

At the same binder weight, BL made from the bentonite-type binder is significantly stronger in coal strength than those prepared with either the old or new standard formulations.

Type of material used to make up Cigarettes that were compared.	Results at 25 gm force and 45 gm force
I. BL* made from bentonite-type binder, 7H 1.2 mg/ft² vs BL* made from old standard binder, 7H 1.2 gm/ft²	Bentonite-type binder significantly stronger
II. BL* made from bentonite-type binder, 7M 1.2 gm/ft² vs BL* made from new standard binder, 7M 1.6 gm/ft²	No significant difference
III. BL* made from bentonite-type binder, 7M 1.6 gm/ft² vs BL* made from new standard binder, 7M 1.6 gm/ft²	Bentonite-type binder significantly stronger
IV. Production-made Parliament using BL based on bentonite binder, 7M CMC 1.2 mg/ft² vs Production-made Parliament using BL based on new standard binder, 7M CMC, 1.6 gm/ft²	No significant difference as expected (see II).

* 100% BL cigarettes made on the Chico maker

00031034

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table VI

Comparison of TPM and Nicotine Delivery

A study of the data indicates that no change in the delivery of TPM or nicotine occurred in either the 100% BL cigarettes or the standard Parliament blends due to the inclusion of bentonite in the BL binder. (Chico-made cigarettes unless noted.)

Pilot Plant Experiment No.	Binder Type	Binder Weight	TPM Mg/cigt.	Nicotine Mg/cigt.
100% BL Cigarettes				
216A	Old std.	1.2	13.3	0.40
B	Bent.	1.2	13.3	0.39
C	Bent.	2.4	13.8	0.36
D	Bent.	0.8	11.1	0.34
230A	Bent.	1.15	11.6	0.93
B	Bent.	1.65	14.5	1.1
Control	Old std.	1.2	14.0	1.07
245-248A	Bent.	1.2	14.6	0.45
B	New std.	1.6	15.9	0.49
Blends - 20% BL, 80% BL-free Parliament				
216A*	Old std.	1.2	20.6	----
B*	Bent.	1.2	21.5	----
230A	Bent.	1.15	23.3	0.97
B	Bent.	1.65	23.1	0.98
Control	Old std.	1.2	24.3	1.09
245-248A	Bent.	1.2	23.7	0.96
B	New std.	1.6	24.5	1.02
245-248A*	Bent.	1.2	27.0	1.12
B*	New std.	1.6	27.3	1.82
Blends - 80% BL, 20% BL-free Parliament				
245-248A	Bent.	1.2	16.5	0.45
B	New std.	1.6	17.3	0.55

* Production-made cigarettes

Φ0000331035

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table VII

Percent Composition of BL Sheet

Components	Old Standard			New Standard			Bentonite			
	Binder Parts	% of binder	% of total sheet*	Binder Parts	% of binder	% of total sheet*	Binder Parts	% of binder	% of total*	% of total sheet*
Bentonite							0.50	21.30	2.27	3.41
Acid (HCl)	0.15	5.65	0.68	0.15	4.76	0.76	0.19	4.26	0.45	.68
CMC 7HP	1.0	37.80	4.54				0.5**	21.30	2.27	3.41
7MP				1.0	31.70	5.07	--			
Propylene glycol	0.5	18.9	2.27	0.5	15.85	2.54	0.25	10.65	1.28	1.70
Pulp	1.0	37.80	4.54	1.5	47.60	7.62	1.0	42.60	4.54	6.82
		100.15			99.91			100.11		
Tobacco			76.00			72.00			76.00	72.00
Moisture			12.00			12.00			12.00	12.00
			100.03			99.99			100.81	100.02
Binder weight, gm/ft^2			1.2			1.6			1.2	1.6
% non-tobacco combustibles			6.81			7.51			3.55	4.11

* 10 gm/ft^2 sheet weight at 12% moisture

** Runs have been made using either 7HP or 7MP CMC

A study of these calculations reveals that a substantial reduction in the non-tobacco combustibles can be realized if the bentonite-type binder is used. If the presently proven bentonite formulation at 1.6 gm/ft^2 is substituted for the new standard formulation at 1.6 gm/ft^2, a reduction in non-tobacco combustibles of 45% can be obtained. If the bentonite formulation at 1.2 g/ft^2 is substituted for the new standard formulation at 1.6 gm/ft^2, a reduction in non-tobacco combustibles of 53% can be obtained.

9E0133000$

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Table VIII

Taste Panel Evaluation

No difference in smoke taste or preference was found when comparing cigarettes containing bentonite BL against cigarettes containing old or new standard BL (100% BL cigarettes; 80% Parliament, 20% BL blend).

Cigarettes Compared (Type of binder and weight)	Results of Test
100% BL Cigarettes (Chico-made)	
216A old standard; 1.2 vs 216B bentonite; 1.2	No difference in taste or preference
273A bentonite; 1.6 vs 273 new standard; 1.6	No difference in taste or preference
Parliament Blends - 20% BL (Chico-made)	
230A bentonite; 1.2 vs 234 new standard; 1.6	No difference in taste or preference
230B bentonite; 1.6 vs 234 new standard; 1.6	No difference in taste or preference
245A-248A bentonite; 1.2 vs 245B-248B new standard; 1.6	No difference in taste or preference
273A new standard; 1.6 vs 273B bentonite; 1.6	No difference in taste or preference
Parliament Cigarettes (Production-made)	
245A-248A bentonite; 1.2 vs 245B-248B new standard; 1.6	No difference in taste or preference

00033103

Source: https://www.industrydocuments.ucsf.edu/docs/xjm40000

Table IX

Annual Binder Cost Calculations

Basis:

1,092,000 lb. CMC/year (1.6 gm binder/ft^2 - 3,448,000 lb, binder/year)

Material:

CMC	$0.620/lb.
Propylene glycol	0.145/lb.
Pulp	0.0574/lb.
Bentonite	0.026/lb.
Hydrochloric acid	0.02025/lb. (anhydrous)

Binder Cost (1.6 gm/ft^2):

	New Standard			Recommended Bentonite		
	%	1000 lb/yr	$/year	%	1000 lb/yr	$/year
CMC	31.7	1092	$677,000	21.3	732	$454,000
Pulp	47.7	1645	94,500	42.6	1468	84,300
Propylene Glycol	15.8	545	79,000	10.8	373	54,200
Acid	4.8	165	3,340	4.2	145	2,940
Bentonite				21.3	732	19,000
Total		3447	$853,840		3450	$614,440

New Standard Binder	$853,840
Bentonite Binder	614,440
Anticipated Annual Savings Using Bentonite Formulation Recommended in this Report	$239,400

00031038

Source: https://www.industrydocuments.ucsf.edu/docs/kjmc0000

Table IX (continued)

Possible future saving based on an optimized bentonite binder (1.2 gm/ft² binder weight)

$$3{,}448{,}000 \text{ lb./yr.} \times \frac{1.2}{1.6} = 2{,}585{,}000 \text{ lb. binder/year}$$

Binder Cost of an Optimized Future Bentonite Binder (1.2 gm/ft²):

	%	1000 lb/yr	$/year
CMC	16.5	427	$265,000
Pulp	39.0	1010	58,000
Propylene glycol	14.0	362	52,500
Acid	4.2	109	2,205
Bentonite	26.5	685	17,800
Total	100.2	2593	$395,505

	Probable Maximum Total Savings
New Standard	$853,840
Optimized Bentonite Binder	-395,505
Anticipated Annual Savings Using Optimized Bentonite Binder	$458,355

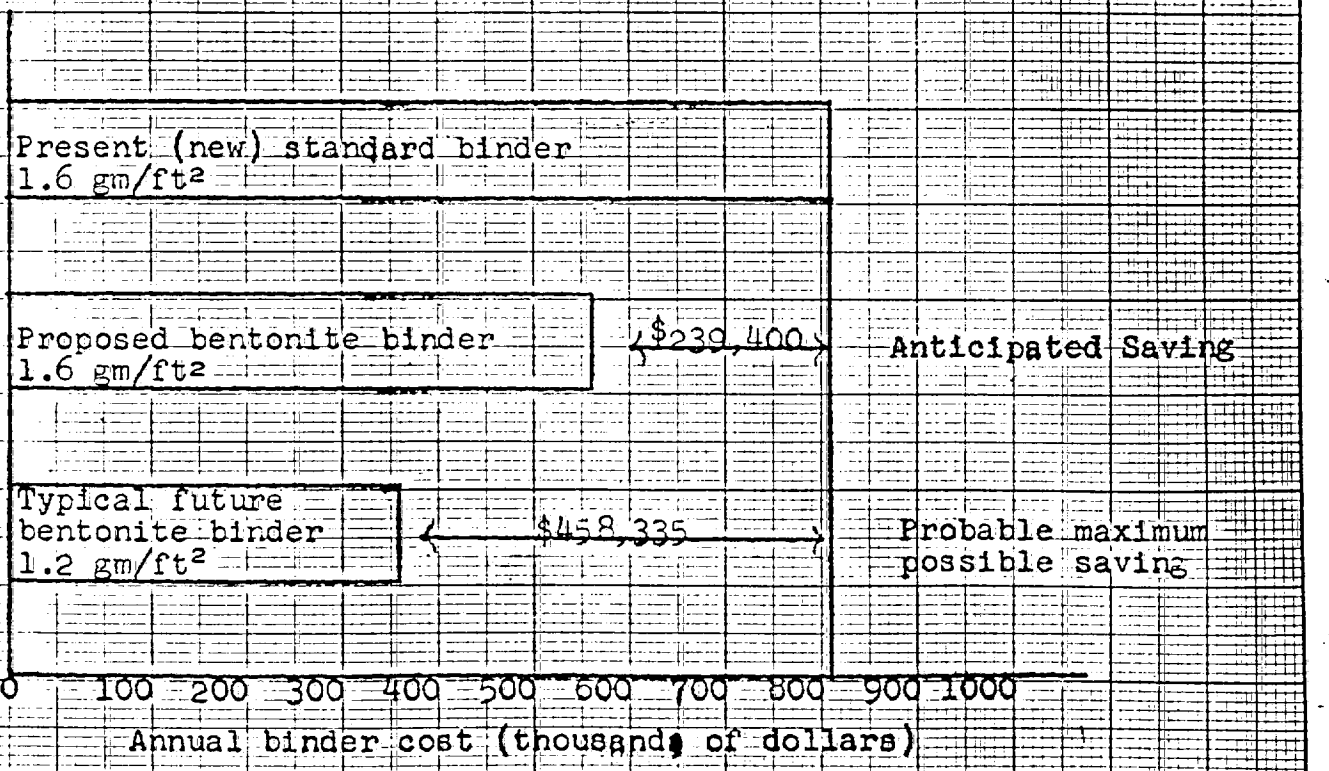
ϕ00031039

Source: https://www.industrydocuments.ucsf.edu/docs/xjmh0000

Table X

Annual Binder Cost Comparison
(See Table IX)

By substituting the proposed bentonite binder at 1.6 gm/ft² for the present standard production binder at 1.6 gm/ft² an annual saving of $239,400 can be realized.



Basis 1,092,000 lb. CMC/year

CMC	0.62/lb.
Propylene glycol	0.145/lb.
Pulp	0.0574/lb.
Bentonite	0.026/lb.
Acid	0.02025/lb.

20 X 20 TO THE INCH KEUFFEL & ESSER CO. 359-10½G MADE IN U.S.A.

D0003310 40

Source: https://www.industrydocuments.ucsf.edu/docs/yjdc0000

Exhibits

ϕ000331041

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Volclay Bentonite

THE SCIENTIFIC ASPECTS OF BENTONITE

In commencing a study of bentonites, as well as other clays, we need to picture the fundamental clay minerals because their pattern influences clay behavior fully as much as the chemical elements of which they are composed.

THE CLAY MINERALS

Pure clay is a mass of mineral fragments, strongly bound together when dry, but separable—when dispersed in water—into myriads of particles so small that many of them are beyond microscopic visibility.

To understand the variable activities of clays, we must start with the invisible world of atoms and molecules and form a mental picture of the way they are assembled to form clay substance. Atoms of silicon, aluminum, and oxygen,* with hydrogen atoms clinging to them, are united in symmetrical patterns to form a molecule; clusters of molecules interlock to form "flake units"; aggregates of flake units form the tiniest particles of what we call clay substance. Literally millions of flake units are needed to make a particle large enough to be visible to the human eye.

Practically the same "materials of construction" form the basis for all clay flakes regardless of the type of clay but the architectural patterns in which these materials are joined are not the same. The difference in pattern is an underlying reason for vividly different properties of the clay itself.

The dissimilar assembly of the atoms permits distinct identification by X-ray methods. Fortunately there are only a few common patterns and they are given different "clay mineral" names. The three principal ones are:

Montmorillonite—the chief clay mineral of bentonite.

Kaolinite—the main constituent of fire clays, china clays, kaolins and ball clays.

Illite—largely found in shales.

There are other clay minerals of minor importance but we will discuss only the first two since they form the basis for most of the commercially useful clays, and for simplicity we will designate montmorillonite as "M" and kaolinite as "K".

*Chiefly those but not exclusively. Magnesium, potassium and iron sometimes occupy positions in the molecule, replacing aluminum.

Copyright 1948, by The American Colloid Company

Molecular Structure

All clays are described as "silicates of alumina" because silicon and aluminum are the primary elements of clay composition. These elemental atoms are assembled in distinct layers of two kinds—silicon-oxygen sheets and aluminum-oxygen sheets. The sheets are combined to form molecules and at this point we observe a radical difference. The M molecule has two silicon sheets with an aluminum sheet sandwiched between them, but the K molecule has only one silicon and one aluminum sheet. M is described as "Si-Al-Si" structure and K as "Si-Al" structure. Certain highly significant effects result from these structural differences.

Groups of molecules are inseparably joined in thin platey particles of definite thickness, but indefinite width and breadth. These are the flake units. The atomic bonds which hold the plate structure together are much stronger laterally than vertically. Laterally, the plates extend until they reach broken edges; vertically they extend only one molecule in thickness. The tops and bottoms of the plates are the basal planes and the thickness is scientifically referred to as the "c-dimension."

Let us conceive a multitude of dry flake units massed together to form a particle of clay substance. Because of their flat shape their plane surfaces are approximately parallel—somewhat like a deck of playing cards flung onto a table. When wetted, they cleave apart, and while not every flake splits away from its neighbors, a large proportion of the M flakes and a less proportion of the K flakes do become individually dispersed.

The cleavage occurs mainly along the basal planes, and therein lies the reason for the greater dispersibility of M. With the Si-Al-Si structure, an Si sheet always faces an Si sheet of the next M flakes above and below it. Like mineral atoms have like electro-chemical charges; consequently the adjacent Si sheets do not attract but may even repel each other. On the other hand a pack of K flakes has Si sheets facing Al sheets of its neighbors, exercising, if anything, an attractive force which resists separation.

Hydration of the Lattice

A layer of water molecules coats the basal

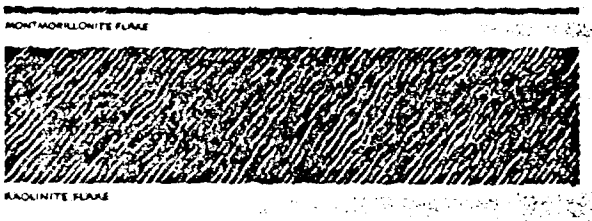
ϕ00033104 2

Source: https://www.industrydocuments.ucsf.edu/docs/xjhx0000

planes of the M flake units, tightly held by a mysterious force. A packet of super-imposed flakes has this layer of water molecules between the flakes even when air-dried; the packet forms what is called a "lattice" structure. When the lattice is wetted more water molecules crowd between the individual flakes, forming layer upon layer in semi-rigid positions, pushing the flakes apart and causing the mass to swell. When the water is removed the mass contracts and the flakes reassume approximately their original spacing.* The movement is only in one dimension, like that of an accordion. It may be repeated indefinitely and is more than simply a curious phenomenon since it leads to correlated activities that become signally valuable in industrial uses.

K flakes on the other hand do not attract layers of water molecules between their basal planes; consequently their spacing is fixed and the mass is not expandible. It requires extremely vigorous mechanical action in water to disperse K into nearly individual flakes. One investigator, using the electron-microscope has estimated the ratios of depth to breadth of clay mineral flake units. His findings indicated a ratio from 1/100 to 1/300 for M and from 1/5 to 1/25 for K. Thus the M flake units have tremendously greater surface area than those of K. The highly magnified colloidal activities of M result from its immense surface area relative to mass.

*A recently discovered process makes it possible to remove the water from swelled bentonite without causing contraction.



Relative Thickness of Flakes of M and K in Water Suspension

The performance of clays is profoundly affected by the kind and number of ions which cluster on the surface of the flakes and in the inter-planar surfaces. Montmorillonite is far more densely populated with attached ions than kaolinite and hence shows greater "ion activity" in water. Ion activity is discussed in a later chapter.

THE CLAY WATER SYSTEM

Clay becomes energized only when wetted. Physicists have formed a hypothetical picture of hydrated clay, being that of a core composed of a flake unit of the clay-mineral surrounded by a hull of water tightly bound to it by electro-static forces. Attached to the clay flake but not an integral part of its crystal structure are swarms of "ions", i.e. electrically charged atoms of other substances which are held by electro-static attraction.

The clay flake with its surrounding atmosphere of attached water molecules and ions is termed by physicists "the micelle." When suspended in a body of water the micelle moves about carrying its inseparable atmosphere with it, somewhat like a solar body in space.

The clay crystal, being composed mainly of aluminum, silicon and oxygen, is slightly acidic in character. The net balance of its electric charges is negative and therefore when suspended in water in an electric field the particles migrate to the anode or positive pole.

That is the broad picture of the water system of most clays, but certain of the effects are intensified when the clay-mineral is montmorillonite and particularly when it is sodium bentonite, to which this discussion will be confined, with Volclay as the prototype.

Hydration

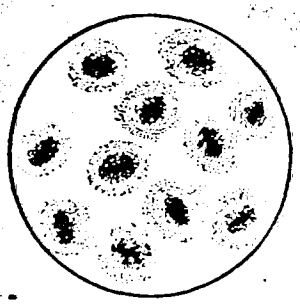
A particle of Volclay bentonite substance is composed of flakes stacked one over the other, their flat sides together, but between each basal plane is a single layer of tightly held water molecules which exists even in air-dried samples. When the particle is wetted, more water molecules press between the flakes forming layer after layer. The distance between the flakes increases until the attractive force of the particle is no longer capable of adding to the thickness of the captive water hull.* Free water then flows between

*The water hull around saturated Volclay particles is so tightly held that it cannot be removed by pressures up to hundreds of pounds per square inch.

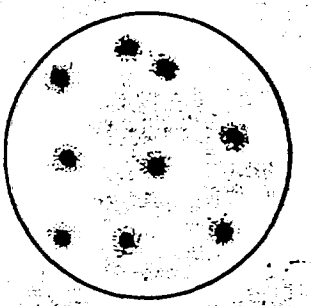
b0003104343

Source: UCSF, https://www.industrydocuments.ucsf.edu/docs/xjmx0000

the semi-rigid water sheaths and the individual micelles float about in the liquid, each retaining its own overcoat of bound water. The micelles do not coalesce as long as the flake retains its electro-chemical charges because all are negative and the flakes mutually repel each other. This is a "disperse system" or sol, and the bentonite particles are "suspensoids".



Montmorillonite flakes (black) with attached water molecules (grey) leaving less "free" water for circulation.



Kaolinite flakes (black) with a smaller hull of water molecules (grey). Ample "free" water, hence no friction to create "viscosity."

When the concentration is sufficiently dilute to allow them "elbow room" the flakes are in almost constant motion, darting about in haphazard zig-zag fashion. This is a characteristic of colloidal sols known as the Brownian Movement and is explained by the kinetic theory of matter which postulates that all molecules are in motion. However, when the sol is allowed to stand quiescent, "gelation" ensues, Brownian Motion decreases and the flakes are held in fixed positions by counteracting electrical forces of attraction and repulsion. In moderately heavy concentrations the mass sets to a semi-solid of jelly-like consistency. Restirring or shaking immediately destroys the jelly-like formation and the sol reverts to its initial mobility, this reversible phenomenon being termed thixotropy. In some industrial uses of bentonite thixotropy is desirable, but often it is disadvantageous.

Electro-Chemical Forces

Montmorillonite molecules do not exist in the simple form of aluminum, silicon and water only; instead, some of the aluminum is replaced by magnesium, ferric and ferrous iron and possibly minor amounts of other ions, these substitutions being part of the fixed crystal structure of the mineral. Aluminum being tri-valent (having three ionic charges) while magnesium and ferrous iron have only two, there is created a valence deficiency. To compensate for this, the flake seizes other ions from outside sources, some of which become loosely attached to the crystal surface while others swarm about in the micelle. Such ions are generally cations (positive sign) and they may be either bases or hydrogen.

Base Exchange

Not all the bases have the same degree of affinity for the clay particle, in fact there is a definite order of preference. When a preferred ion is present in the surrounding water, it replaces an ion of a lower order in the micelle. Physicists have compiled this sequence: Calcium, Magnesium, Potassium, Hydrogen, Sodium, Lithium.

Calcium dominates and will replace any of the other bases below it in the list and that fact accounts for the decided changes that occur in sodium bentonite suspensions when a calcium-containing compound is added to the water.

The type of replaceable base originally dominant in the clay is probably responsible for the magnitude of its swelling and the amount of water which it will absorb. Sodium induces high solvation, swelling and suspendibility; when it is replaced by calcium the swelling of the bentonite is greatly reduced. Natural calcium bentonites such as occur in the South (for example, Panther Creek bentonite) are practically non-swelling.

Measuring Base Exchange

The exchangeable bases of clays are determined by a laboratory procedure of leaching and analysis, and the amounts being expressed in milli-equivalents per 100 grams of clay. Certain of the physical activities of the clay can be predicted from the results of such a test. Comparative figures of three bentonites and two other clays are shown in Table 1.

Effect of Electrolytes

Electrolytes are substances—they may be acids, bases or salts—which are dissociated or liberated in water to form charged particles or ions. The

0000331044

Powered by Document Cloud Solutions Copyright 2008

TABLE 1. EXCHANGEABLE METALLIC BASES In Milli-equivalents per 100 grams

	BENTONITES			OTHER CLAYS	
	Volclay Wyoming	*Panther Creek Mississippi*	*Lovite Nevada*	*Ohio Plastic Fire Clay*	*Kentucky Ball Clay*
Calcium	22.0	64.7	51.5	5.2	7.1
Sodium	85.5	0.4	33.6	0.4	0.5
Potassium	5.0	2.8	1.1	0.5	0.4
Magnesium	1.0	1.0	19.1	1.3	3.8
Sum	89.2*	60.1*	78.1*	7.4	11.8

*Corrected for sulphates.

ions thus diffused are negatively or positively charged and they may carry one, two, three or more ionic charges (uni-valent, di-valent, tri-valent, etc.). Ionizing substances may act through simple contact with merely slightly moist bentonite, but they act more intensively in sols and for the purposes of this article we will consider only the sol or disperse system.

The influence of electrolytes on clay-water systems of ordinary clays has been the subject of a vast amount of research by noted soil chemists and colloid authorities and in the last few years similar work has been initiated with bentonite suspensions. Sodium bentonite is particularly susceptible because of its stronger electric charges; the greater surface area of its flakes; the sponge-like character of its lattice which permits the free ingress and egress of ions which may be present in the water; its suspendibility and mobility in water which gives more opportunities for collision with other floating ions.

Electrolytes change the character of bentonite suspensions in many respects; under some conditions they thicken it, under others they make it thinner, reducing the viscosity and increasing filterability. The results are determined by three principal factors; the kind of electrolyte, the concentration of bentonite to water and the concentration of electrolyte relative to bentonite.

Mono-valent ions are only mildly influential; di-valent ions much more effective and tri-valent ions tremendously more so, the relation being sometimes stated at 1-30-1000. An excess of either negative or positive ions depolarizes the bentonite particles so that they no longer repel each other and coalescence and floculation ensues. It is not scientifically established that depolarization is the only cause; "desolvation" or a change in the bound water of the micelle, may also be responsible and could occur through the substitution of ions having less water holding capacity. The size of the ion may also be an influence, hydrogen for example being very small and therefore numerically more hydrogen atoms can be packed into the channels between the flakes. Ions possessing thick water hulls, when attached to the outer surface of the particle, are held further away from it, from which various deductions can be made.

Clay water systems may contain both positively and negatively charged electrolytes and those with high and low valences and they may modify each other. The bentonite itself is an electrolyte and when complicated by other electrolytes in the water, the results are predictable only in a general way and are best ascertained by empirical experiments.

Except for a few general rules such as the dominance of either calcium or sodium, the chemical analysis of a bentonite sample does not permit exact evaluation of its properties of swelling, gelling and suspending even in distilled water. The data on this subject is constantly being accumulated and sifted; the broad path is fairly clear but it is crossed by devious trails which have not yet been mapped.

Volclay and Panther Creek bentonite are produced only by

AMERICAN COLLOID COMPANY, Merchandise Mart Plaza, Chicago 54

0003310457

Source: https://www.industrydocuments.ucsf.edu/docs/xxxxxxx

Particulate Matter Inhalled Per Day by an Average Individual

I. Reference Air Pollution Handbook (p. 2-43)

Concentration of Suspended Particulate Matter in the Atmosphere of a Number of Communities

	Minimum	Maximum	Mean
	Micrograms/Liter of Air		
Baltimore - Downtown	0.21	1.72	0.87
- Industrial	0.05	1.46	0.38
Cincinnati - Industrial	0.01	1.98	0.42
- Residential	0.01	1.30	0.28
Donara, Pa.	0.00	2.50	0.74
Los Angeles, Detroit San Francisco, Washington	0.25	0.47	0.51

II. J. E. Hardcastle's report of April 14, 1958

Particulate matter inhaled by an average individual is based on the following:

$$\text{Volume of air taken in per day} = \frac{(15 \text{ breathes})}{\text{min.}} \frac{(60 \text{ min.})}{\text{hr.}} \frac{(24 \text{ hrs.})}{\text{day}} \frac{(0.8 \text{ liter})}{\text{breath}} = 17280 \text{ liters/day}$$

Amount of suspended particulate matter inhaled per day

	Micrograms/day		
	Minimum	Maximum	Mean
Baltimore - Downtown	363.0	2975	1508
- Industrial	86.5	2520	657
Cincinnati - Industrial	17.3	3520	727
- Residential	17.3	2250	484
Donara, Pa.	0.0	4320	1280
Los Angeles, Detroit San Francisco, Washington	432.0	81.3	882

Φ00331046

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Exhibit 3

B I O L O G Y O F B E N T O N I T E

by

S. Solomon

Richmond, Virginia

September 7, 1960

ϕ00033104

Source: https://www.industrydocuments.ucsf.edu/docs/jmkd0000

SUMMARY

Smoking cigarettes containing bentonite probably will not constitute any more of a health hazard than does present day smoking of non-bentonite containing cigarettes. This statement is based upon the fact that analysis of smoke from bentonite containing cigarettes does not contain any more materials traceable to the bentonite than does smoke from controls. Bentonite is, moreover, used in certain medical preparations and procedures. A health hazard does exist when bentonite is chronically ingested in the diet at a level greater than 1/2 per cent of the diet. Breathing air heavily laden with bentonite dust constitutes another type of health hazard.

Φ00031048

Source: https://www.industrydocuments.ucsf.edu/docs/ynbl0000

PHILIP MORRIS INCORPORATED

INTER-OFFICE CORRESPONDENCE

RICHMOND, VIRGINIA

To: Dr. L. S. Harrow Date: September 7, 1960

From: S. Solomon

Subject: Biology of Bentonite.

I. INTRODUCTION:

This report covers selected papers found in the literature of the past ten years which are concerned with the biological action of bentonite. Since reports concerning bentonite are few, the biological effects of the related substances, talc and kaolin, are also considered for suggestive data. In evaluating health hazards, it is necessary to look at many possible pharmacological effects, such as acute toxicity, synergism and antagonisms to other pharmacological agents, antigenic properties, chronic effects, and others. Only in two areas, the production of respiratory pathology and liver pathology has bentonite been involved as a pathologic agent. It will be seen that the reports of these effects probably do not have very much meaning in terms of a bentonite hazard resulting from smoking cigarettes using this material as an humectant.

II. RESPIRATORY HAZARDS:

If dust particles of a great many types are inhaled in adequate concentration, there occurs a series of reactions between the dust particles and the animal.(1) The particles impinge on the cellular lining of the lung across which gaseous exchange takes place. Some of these particles will be passively moved to the small conducting airways, the bronchiales, where by ciliary action, they will be removed. Other particles will be engulfed by specialized cells, macrophages. They can either be moved to the bronchiales and be eliminated by the cilia as with free dust particles, or they can accumulate in intracellular and lymphatic spaces in the pleural region. When the latter occurs the dust laden macrophages (conglomerate), and became walled off somewhat by biological processes whereby an amorphous mass of gelatin-like material comes to embed them (hyalinization) and fibrous masses are laid down in and around them (collagenization If exposure is severe, tissue distruction may occur (necrosis). In any event the appearance of these particle-filled nodules gives rise to disease entities called pneumoconiosis, of which the most well known is silicosis caused by silica dusts. It is of interest that in the induction of a pneumoconiosis, small particles constitute the greatest danger since they travel the furthest down the respiratory tree.(2)

0000331049

Source: https://www.industrydocuments.ucsf.edu/docs/[illegible]

The evidence favors the view, that at high enough concentrations, bentonite can induce pneumoconiosis. Rombola and Guardascione(2) report a number of cases of this disease among bentonite workers in the Parma district (Italy). The bentonite concerned contained about 30% free silicon dioxide as vitreous silica and as the mineral betacristobalite. They found a good correlation between the intensity of dustiness and the frequency of pneumoroniosis. The intensity of the danger appeared to be far more important than the duration as shown by the following facts. 1. Miners of bentonite had a lesser frequency of the disease than did workers in processing and refining plants. Dust counts were higher in the latter. 2. In comparison of two plants, the disease was more frequent in the plant with the higher dust hazard. 3. In the plant with the higher dust hazard, the work duration was shorter than in the other, before onset of the symptoms.

It has been reported that intratracheal injection of bentonite solutions results in pneumoconiosis in rats.(3) As pointed out (see report by Solomon on XIII Int. Cong. of Indust. Health) the doses given were massive. Furthermore, pathology has been found to be induced by talc(4) and by kaolin (4, 5, 6, 7,). As with the experiments on rats, a high dust atmosphere or high dosages of the substances has been required to produce effects. The cases reported occurred in people working as miners or in industries where these substances were used.

III. SOME OTHER EFFECTS OF BENTONITE:

Wilson has reported that a diet containing 25% bentonite causes marked changes in the liver characterized by, 1. fatty liver, 2. fibrosis, 3. pigmentation and 4. formation of hepatomas (8, 9, 10). He suggested that these results could be explained on the basis of adsorption of essential growth factors by bentonite. On diets of 0.5 to 3% bentonite, rats are unable to accumulate vitamin A added to the diet by the liver (11, 12). On a basal diet and bentonite alone, liver weight was down although there was no reduction in body weight. One may again note here the high concentrations which were used.

In isolated frog hearts, the amplitude of the beat has been restored by bentonite after the heart beat was reduced by low calcium or high potassium. It was suggested that this was a result of the high surface activity of the bentonite.(13)

IV. SOME USES OF BENTONITE AND TALC:

Despite what seems to be a health hazard, bentonite, talc, and kaolin are used in medical procedures. Thus kaolin is used

0000331050

Source: https://www.industrydocuments.ucsf.edu/docs/fyhd0000

in the treatment of chronic spontaneous collapse of the lung[14] in order to induce the laying down of fibrous tissue. It has further been shown that such treatment does not lead to detectable changes in lung function.[15] Both talc and bentonite have been used in X-ray examination of the bronchial tree.[16]

V. ESTIMATION OF POSSIBLE HEALTH HAZARD OF THE USE OF BENTONITE AS AN HUMECTANT:

The evidence is strong that chronic high level intake of bentonite by oral and respiratory routes constitutes an health hazard. Despite this apparent danger, drug companies use bentonite in various medical preparations (donnagel,[17] for example.

To evaluate the respiratory hazard, however, one should look at the dust data of smokes obtained from bentonite containing cigarettes (see Table 1). It has been found that the bentonite containing cigarettes contains no more silica or aluminum compounds in smoke than do control cigarettes, nor is the total organic content greater. Moreover upon microscopic examination of the smoke, bentonite was not detectable.[18] With respect to the biological effects discussed above, it seems reasonable, therefore, to conclude that addition of bentonite to cigarettes does not constitute any more of a health hazard than does smoking of cigarettes produced by methods now in use. The quality and health hazard may even be improved since there is a possibility that bentonite may adsorb certain compounds which are irritants.[19] Work, however, would be required to establish this latter possibility.

/mar

S. Solomon/MAR

Φ00031051

Source: https://www.industrydocumentslibrary.ucsf.edu/tobacco/docs/#id=

TABLE 1.

COMPARISON OF CONCENTRATIONS IN EXPERIMENTAL STUDIES IN BENTONITE

SOURCE	CONCENTRATION OF INORGANIC MATTER	REF. NUMBER
Diet	25% by weight	8, 9, 10
Diet	0.5 to 3% by weight	11
Intratracheal injection	40 mg. in a single injection	3
Control cigarettes	860 mmg./liter of smoke	19
Bentonite cigarettes	674 mmg./liter of smoke	19

Φ00033105Z

Source: https://www.industrydocuments.ucsf.edu/docs/[illegible]

LITERATURE CITED

1. Gross, P., A.M.A. Arch. Ind. Health 19:426, 1959

2. Romboli, G. and Guardascione, V., Med. de. Lavora. 46:480-97, 1955

3. Nadudvary, G. and Balkanyi, N., Abstract #29-5; XIII Int. Cong. Ind. Health, 1960

4. Prevost, E. M., Medicine d'Usine (Paris) 14;77, 1952

5. Cummins, G. E. L., Aun, Y. S. and Davies, T. A. L. Med. J. Malaya 12:613, 1958

6. Hale, L. W. and Gough, J., Br. J. Indust. Med. 13;251, 1956

7. Schmidt, K. G. and Luchtrath, H. Beitc F. Silikose-Forschung 58:3, 1958

8. Wilson, J. W., J. Nat'l Cancer Inst. 14;56,1953

9. Wilson, J. W., J. Nat'l Cancer Inst. 14; 65, 1953

10. Wilson, J. W., Ann N. Y. Acad. Sci. 57: 678, 1954

11. Laughland, D. W. and Phillips, W. E., Can. J. Biochem. and Physiol. 32; 593, 1954

12. Laughland, D. W. and Phillips, W. E., Can. J. Biochem. and Physiol. 32; 610, 1954

13. Marshall, J. M. and Andrus, E. C. Proc. Soc. Exp. Biol. Med. 82; 228, 1953

14. Joynt, G. H. and Laird, R. C., Diseases of the Chest 34; 514, 1958

15. Paul, J. S., Beattie, E. J. and Blades, B. Thorac. Surg. 22; 52, 1951

16. Rose, Y. and Remy, J., Ann. Otolar. (Paris) 71:324, 1954 (not read by S. Solomon, but title self-explanatory)

17. Winfield, I. W., Am. J. Gastroent 31; 438, 1959

Φ0003310S3

Source: https://www.industrydocuments.ucsf.edu/docs/pmkx0000

LITERATURE CITED (continued):

18. Holmes, J. C. report to L. S. Harrow of August 10, 1960

19. Weil-Malherbe, H. and J. Weiss,
J. Chem. Soc. 2164; 1948

0000331054

Source: https://www.industrydocuments.ucsf.edu/docs/jpmk0000

PHILIP MORRIS INCORPORATED

INTER-OFFICE CORRESPONDENCE

RICHMOND, VIRGINIA

To: Mr. H. Merritt Date: June 15, 1960

From: L. S. Harrow

Subject: Proposed Coroborative Proof of Innocuousness of Bentonite.

With reference to the suggestion made by Dr. Solomon that some simple animal tests might be made which could show the lack of respiratory tree ill effects produce because of bentonite incorporated in filler, I have discussed this matter with Dr. Kenneth Morgareidge of FDRL and Dr. J. L. Radomski, pharmacologist, at the University of Miami School of Medicine. Both consultants concur in the opinion that (1) the demonstration of relative freedom from debris of the particulate matter collection pad interposed in the smoke stream of a bentonite treated cigarette relative to that interposed in the smoke stream of a control cigarette constitutes the most practical proof of the innocuousness of the bentonite addition. (2) a coroborative study of animal respiratory tree after exposure to smoke from bentonite and control cigarettes would yield observable differences only if these tests were carried out using inordinately high levels of bentonite over long periods of time and in large animal populations. They both feel that this test would be extremely expensive, time consuming and possibly inconclusive.

For this reason, I recommend that we go the rest of the way on this problem with the data presently in hand, unless, we reach the stage of a major commitment by the company and a major objection is raised to our present evidence. I will, of course, explore this matter further if you desire.

LSH:mar
cc: Dr. R. B. Seligman
Dr. H. Wakeham

Lee

2000331055

Source: https://www.industrydocumentslibrary.ucsf.edu/tobacco/

PHILIP MORRIS INCORPORATED

INTER-OFFICE CORRESPONDENCE

RICHMOND, VIRGINIA

To: Mr. Henry Merritt Date: July 12, 1960

From: L. S. Harrow

Subject: Bentonite.

On my recent visit to the University of Miami School of Medicine, I discussed the "Proof of Safety" problem of bentonite with Doctors Deichmann and Radomski. They will, at our request, forward to us very shortly a detailed proposal - plan for the investigation necessary to show any toxicity of bentonite dust administered through the respiratory tract. This was done so that you will be prepared if the necessity arises to accumulate required data in support of bentonite usage. I have left a small part of the bentonite files with them, but they will return these very shortly. Meanwhile, I am returning the rest of your file to you.

LSH:mar

Lee

$0003310$6

Source: https://www.industrydocuments.ucsf.edu/docs/

Exhibit 4a

Food and Drug Research Laboratories
INCORPORATED

Maurice Avenue at 58th Street
Maspeth 78, New York City
Telephone TWining 4-0800
Cable: Foodlabs, New York

March 16, 1960

COPY

Mr. J. C. Holmes
Philip Morris, Inc.
McComas Research Center
P. O. Box 3 D
Richmond 6, Virginia

Dear Joe:

In answer to your letter of March 9th, we will look forward to receiving samples of cigarettes for aluminum analysis of smoke as soom as you have them ready.

Meanwhile, you have asked us to comment on the possible significance to the smoker of minute traces of Bentonite inhaled with the smoke of cigarettes made from "BL" containing the mineral. Strictly speaking, of course, this raises the question of silica since Bentonite is an aluminum magnesium silicate. Silaceous substances absorbed by the lung are trapped in the proximal lymph nodes where they set up a marked foreign body reaction due, in the opinion of some authorities, to the acid character of silicic acid. This condition is often referred to as "silicosis." It is a common disease among workers in certain mines where silica dust is prevalent.

Actually, the literature appears to offer little information on the minimum level of exposure to silicates which may cause clinical symptoms of silicosis. At least, a much more detailed search would have to be made. However, it seems clear from our investigation to date that the process is cumulative since silica-bearing particles once trapped remain in the nodes for the life-time of the individual.

Another point requiring further study is the differences between various silaceous materials in their ability to induce the disease. Many qualitative differences have been reported and we have no information on the history of silicosis being produced by the Bentonites.

From a practical standpoint, we rather doubt that the few micrograms inhaled with the smoke from each cigarette would deposit sufficient silica as Bentonite in the lungs of the smoker to be significant in comparison with the relatively enormous amounts constantly being inhaled from the polluted atmosphere in which we live. Almost all dusts have more or less silica content.

0000331057

Source: https://www.industrydocuments.ucsf.edu/docs/gmhc0000

We suggest that you consider these comments as preliminary to a more careful evaluation which should be postponed until after your own exploratory work is completed and until after we have the results of the aluminum analyses on the smoke which we will conduct. If the levels are found to be significant, we can institute a thorough literature search on the subject.

Cordially yours,

FOOD and DRUG RESEARCH LABORATORIES, Inc.

Assistant Director

Dr. Kenneth Morgareidge:rfm

0000331058

COPY

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

CABLE "SLEINAD"

Exhibit 4b

WHITTAKER

ESTABLISHED 1890

WHITTAKER, CLARK & DANIELS, INC.

WORTH 4-2060 · 100 CHURCH STREET · NEW YORK 7, N. Y.

May 26, 1960

Mr. Henry B. Merritt
Development Division
Research & Development
Philip Morris Inc.
P.O. Box 1895
Richmond 15, Va.

Dear Mr. Merritt -

On the telephone the other day you asked me for any clinical data or any information that we had regarding Bentonite, and I have done my best to locate some of this material and am sending to you with this letter various re-prints and write-ups on feeding test and animal foods; to rats, lambs, dogs, and mice for what value they are. I hope that this material will help you.

Whittaker, Clark & Daniels, sell in LCL lots, out of the warehouse, a considerable amount of Bentonite to various pharmaceutical, food producing and cosmetic customers. I can list, The Pure Pack Pharmarcal Company, the Mifflen McCambridge Company of Philadelphia, New York Quinine, R. H. Macy's Pharmaceutical Department, Lambert Hudnut, Colgate, Sterling Drug, Stein hall, Strong Cobb & Arner Co., Rexall Drug Co., H.R. Laboratories, Johnson & Johnson, The Upjohn Co., The Borden Chemical Co., Mckesson & Robbins, Whitehall Laboratories, Avon Products, Nutrilite Products Co., R.H. Miller Co., Whittaker Drug and the Syracuse Pharmacal Co., are a partial list of customers using Bentonite which could have a pertinent bearing.

As a final and compelling argument you might use the fact that in the Feburary 2, 1960 issue of the Federal Register under the Food Additive Amendment to the Food and Drug Law, that Bentonite was listed as a material which was generally regarded as safe and not limited in any way.

Ordered 3PW

Very truly yours,

WHITTAKER, CLARK & DANIELS, INC.

S. R. Mountsier, Jr.
Manager
Technical Service Laboratory

SRM/fpm
Encs.

IMPORTERS · MANUFACTURERS · EXPORTERS

MINERALS, COLORS, PIGMENTS

0000331059

Source: https://www.industrydocuments.ucsf.edu/docs/yqbc0000

PHILIP MORRIS INCORPORATED

Exhibit 5

INTER-OFFICE CORRESPONDENCE

RICHMOND, VIRGINIA

To: Mr. H. B. Merritt

Date: August 4, 1960
Reissued August 15, 1960

From: R. B. Seligman

Subject: Coal Strength Measurement of 100% BL Cigarettes (Bentonite Binder)

On August 1, 1960, Mr. W. G. Lloyd relayed the following information to me by telephone. The data were obtained by measuring the coal strength on special 100% BL samples which we at the Research Center submitted to the Quality Control Laboratory for evaluation. Two samples were submitted: No. 273A, a control sample made from pilot plant BL which was manufactured with the normal binder formulation, and No. 273B, an experimental pilot plant BL made with 50% bentonite replacing CMC in the binder formulation. Two types of coal strength measurements were made by the Quality Control Laboratory; one using the force gauge which measures the force required to remove the ash from the burning cigarette, and the other an impact gauge test where the burning ash is knocked from the cigarette by striking the cigarette with a given force at the distance of four millimeters behind the burning coal. The results of these two tests are listed in the two tables below:

Force Gauge Test

Sample Code	g of force*	% weak[1]	% very weak[2]	Number of cigts. tested
273A	26.78	13	2	100
273B	29.04	9	3	100
273A	28.36	2	0	50
273B	29.44	4	1	50

1 "Weak" described as requiring 18 g of force or under to remove coal.

2 "Very weak" described as requiring 14 g of force or under to remove coal.

* All the values recorded in this column were extremely high for 100% BL cigarettes.

Impact Gauge Test**

Sample Code	% coals removed in 100 cigts. test	% coals removed in 50 cigts. test
273A	83	82
273B	67	70

** For comparison, this impact test removes 35% of the coals from a Parliament cigarette.

ϕ0003310600

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

By copy of this memo I am informing Mr. Lloyd of my recounting of his telephone conversation. Should any of the information presented in this memo be incorrect, I would appreciate his contacting me immediately.

/hj
cc: Mr. W. G. Lloyd

RBSelgmo

Φ00331061

Source: https://www.industrydocumentslibrary.ucsf.edu/tobacco/

Exhibit 6.

Mr. H. B. Merritt

September 12, 1960

C. E. Maxwell, Jr.

Panel Tests Showing the Effect of Bentonite on Smoke Flavor
(All cigarettes Chico-Made Unless Noted)

A. 100% BL cigarettes coded 216-78A (old std. 1.2 GPF) versus 100% BL cigarettes coded 216-78B (1.2 GPF special binder with Bentonite):

A triangle difference smoking test did not show any significant differences (8/28 correct) in taste between the cigarettes.

B. 100% BL cigarettes coded 216-78A (old std. 1.2 GPF) versus 100% BL cigarettes coded 216-78C (2.4 GPF special binder with Bentonite):

A triangle difference smoking test did not show any significant differences (8/28 correct) in taste between the cigarettes.

C. 100% BL cigarettes coded 216-78A (old std. 1.2 GPF) versus 100% BL cigarettes coded 216-78D (0.8 GPF special binder with Bentonite):

A triangle difference smoking test showed the cigarettes significantly different (15/29 correct) in taste at the 5% level of significance, but the nature of the difference was not clearly defined. Each cigarette was equally preferred and both cigarettes were described as strong and irritating. We recommend an additional test on these cigarettes in order to establish this finding or to determine the difference.

D. Parliament cigarettes containing 80% Parliament filler (BL free) plus 20% BL control (N std. 1.6 GPF) filler versus Parliament cigarettes containing 80% Parliament filler (BL free) plus 20% BL coded 230A (1.2 GPF special binder with Bentonite) filler (no filters):

A significant triangle difference smoking test did not show any significant differences (11/29 correct) in taste between the cigarettes.

Φ0003310 62

Source: https://www.industrydocuments.ucsf.edu/docs/xjax0000

E. Parliament cigarettes containing 80% Parliament filler (BL free) plus 20% BL control (N std. 1.6 GPF) filler versus Parliament cigarettes containing 80% Parliament filler (BL free) plus 20% BL coded 230B (1.6 GPF special binder with Bentonite) filler (no filters):

A triangle difference smoking test did not show any significant difference (9/28 correct) in taste between the cigarettes.

F. Production made Parliament cigarettes Coded 460 (BL binder N std. 1.6 GPF) versus Parliament cigarettes coded 459 (BL binder with Bentonite 1.2 GPF):

Individually or combined, the results of two triangle difference smoking tests did not show any significant differences (19/56 correct) in taste between the cigarettes.

G. 20% Parliament filler (BL free) plus 80% BL filler coded 245-48B cigarettes versus 20% Parliament filler (BL free) plus 80% BL filler coded 245-48A containing 1.2 GPF special binder with Bentonite (no filters):

A triangle difference smoking test did not show any significant differences (8/21 correct) in taste between the cigarettes.

H. 100% BL cigarettes coded 273B (N std. 1.6 GPF) versus 100% BL cigarettes coded 273A (1.6 GPF special binder with Bentonite):

A triangle difference smoking test did not show any significant differences (8/22 correct) in taste between the cigarettes.

Our judges did not find any specific difference which they agreed upon in these tests. We conclude that the lack of unanimity means there is no large difference between cigarettes made from Bentonite binder BL when compared to old binder or new standard binder BL. If a change is to be made in production, we recommend additional full pack hand-out tests to determine if a build-up factor is involved.

C. E. Farwell Jr.

/jos

cc: Dr. R.B. Seligman
Mr. W.H. Danker

Φ0000331063

Source: https://www.industrydocuments.ucsf.edu/docs/ynm20000

Exhibit 7

WATSON LEAVENWORTH KELTON & TAGGART

100 PARK AVENUE

NEW YORK 17

LESLIE D. TAGGART
ELMER R. HELFERICH
NORMAN N. SCHUTTLER
JOHN T. KELTON
JOHN R. JANES
GEORGE P. KRAMER
ROBERT C. NICANDER

NICHOLAS JOHN STATHIS
WILLIAM H. VOGT III
DONALD J. GOODELL
HERBERT BLECKER

LEONARD A. WATSON (1930-1960)
ELLIS W. LEAVENWORTH (1930-1958)

MURRAY HILL 3-4221

CABLE ADDRESS "WATSOLAW"

August 12, 1960

Mr. Henry B. Merritt
McComas Research Center
Philip Morris Incorporated
Richmond 6, Virginia

Re: Use of Bentonite in BL
Our File 582-152

Dear Mr. Merritt:

I have made a preliminary patent survey with respect to the proposal to embody bentonite in the adhesive in the BL process. The below table, for which you supplied the data, gives representative examples of the proposed composition employing bentonite and the present practice respectively:

	Proposed	Current
Tobacco pulp	42.6	47.65
CMC	21.3	31.75
Propylene glycol	10.6	15.85
Acid	4.2	4.75
Bentonite	21.3	
	100.00	100.00
pH	3.5 to 5	2.6 to 2.8

The above composition employing bentonite and CMC in a 1 : 1 ratio gives a tensile strength substantially as good as the current product and of course is much cheaper. Also the product has greater ash strength.

I understand the higher the acid content (and the lower the pH) the greater the wet strength and conversely, of course. Stated otherwise the sodium carboxymethyl cellulose (NaCMC) is water-soluble, whereas the acid type referred to as cellulose glycolic acid (HCMC) is water-insoluble. There are

Φ0003310641

Source: https://www.industrydocuments.ucsf.edu/docs/jnhf0000

I presume intermediate conditions. I understand that Philip Morris measures the property involved in terms of wet strength or more specifically the ratio of wet strength to dry strength in relation to the pH. However, the patents with which we are probably most concerned discuss the material as being water-soluble or insoluble and it will be important for us to determine whether the proposed Philip Morris composition is water-soluble within the meaning of certain patents to Frankenburg. I understand that in the compositions employing bentonite it is desired to work toward the higher pH because, although the wet strength increases as the pH decreases, the adhesiveness decreases.

My investigation of the prior art thus far has been limited to such patents as we have in our present files and particularly patents to General Cigar (Frankenburg) and American Machine & Foundry. Several propose to add bentonite or Kaolin to the adhesive base. I call attention in this respect to the following (copies enclosed):

	Frankenburg et al.	No. 2,592,553 - Apr. 15, 1952
	Frankenburg	No. 2,592,554 - Apr. 15, 1952
	Hungerford et al.	No. 2,734,510 - Feb. 14, 1956
(Br.)	American Machine	No. 698,948 - Oct. 28, 1953

The Frankenburg patent -553 proposes to add to the NaCMC bentonite in a proportion of 1% to 2% by weight based on the weight of the dry tobacco. The Frankenburg patent -554 describes the use of an acid polysaccharide and more specifically sodium or potassium alginate and includes one example in which bentonite is added in the ratio of 1 part bentonite to 4 parts potassium alginate.

The Hungerford patent (AMF) mentions the addition of Kaolin or Fuller's earth and has two examples in which Kaolin is mixed with NaCMC in a ratio of 1 : 2.

The British patent is concerned particularly with the forming of cellulose glycolic acid from the CMC salt in which for example NaCMC is extruded in small filaments into an acid, but the patent goes on to give illustrations of the use of the acid CMC product and states that there may be mixed with it Kaolin, bentonite and Fuller's earth, and describes that the material may be used in producing a reconstituted tobacco sheet.

0003310650

Source: https://www.industrydocuments.ucsf.edu/docs/xxxxxxx

Each of the Frankenburg patents must be seriously considered on the question of infringement. One critical factor in determining whether certain claims of these two patents are infringed is that of whether the proposed Philip Morris composition embodies a "water-soluble acid polysaccharide compound" in the case of patent -554, or a "water-soluble cellulose derivative" in the case of patent -553.

The below claims are representative of those which must be considered on the question of infringement, the claim 1 being from patent -553 and claim 15 from patent -554:

> "1. A tobacco product adapted for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble cellulose derivative having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight of said cellulose derivative is dissolved in water, said cellulose derivative functioning to hold the particles of said tobacco together as a coherent mass."

> "15. A tobacco product suited for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not more than 20% by weight of said tobacco, of a water-soluble acid polysaccharide compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at 25° C. when not more than about 5% by weight of said polysaccharide is dissolved in water, said polysaccharide functioning to hold said dry-ground tobacco as a coherent mass."

0000331066

The Frankenburg patents are both directed to a process and product in which the ground tobacco is mixed throughout the adhesive matrix as distinguished from the BL process in which a more or less sandwich type of product is made, and

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

there is some basis for arguing that the patents do not cover a BL type of sheet. However, the Frankenburg claims in question are rather broad in this respect in stating that the adhesive serves to hold the tobacco together as a coherent mass.

Another question may be as to whether the Philip Morris adhesive material has a viscosity of at least 1500 centipoises at 25° C. when not more than about 2% by weight is dissolved in water (see claim 1 above), or in the case of claim 15 above when not more than 5% is dissolved in water. This is a technical question for Philip Morris to determine.

The main question, however, is whether the proposed composition is water-soluble. The patents and literature seem to indicate very clearly that the definitely acid type CMC is water-insoluble and the CMC salt is soluble, but I do not find much enlightenment in the patents on the intermediate compounds. However, I refer you to column 3 of Frankenburg -553 where he purports to define what he means by "water-soluble derivative of cellulose". The AMF patents refer to the CMC salt in water as a solution and to the acid CMC as an aqueous dispersion (see e.g. patent -510, col. 4, lines 29-42). I enclose herewith a copy of an article in Industrial & Engineering Chemistry, for October 1945, pages 943-7, containing an article by engineers from Hercules Powder entitled "Carboxymethylcellulose. Uses and Applications" which describes the sodium salt for example as soluble in water and also refers at various points to the "water-insoluble alkali soluble type of carboxymethylcellulose" without defining insofar as I have noted the composition of the water-insoluble type. I do not know, however, that the above article adds much to the Hercules brochures to the trade which you have.

It may be that we can attack the validity of the Frankenburg patent claims and I have some prior art and tentative thoughts on that phase but it seems to me the major question at the moment is the matter of whether the proposed Philip Morris composition is water-soluble and to what degree. That, I believe, is primarily a technical point which Philip Morris should investigate and report on before we can formulate an opinion as to whether the Frankenburg patents would be infringed.

Source: https://www.industrydocuments.ucsf.edu/docs/jnwd0000

Mr. Henry B. Merritt ... 5 August 12, 1960

I shall defer any further investigation or study of the matter until I receive your views on the above.

Sincerely,

E. R. Helferich

Encs.

cc. Dr. Helmut R. Wakeham

ϕ00033106 8

Source: https://www.industrydocuments.ucsf.edu/docs/xjnc0000

Patented Apr. 15, 1952 2,592,553

UNITED STATES PATENT OFFICE

2,592,553

TOBACCO PRODUCTS AND PROCESSES THEREFOR

Walter G. Frankenburg, Millersville, Pa., and Paul W. Garbo, Freeport, N. Y., assignors, by direct and mesne assignments, to General Cigar Co., Inc., New York, N. Y., a corporation of New York

No Drawing. Continuation of application Serial No. 720,682, January 7, 1947. This application January 30, 1950, Serial No. 141,357

18 Claims. (Cl. 131—15)

1

This application is a continuation of copending application, Serial No. 720,682, filed January 7, 1947 and now abandoned.

This invention relates to tobacco products adapted for smoking, and more particularly to products comprising tobacco in comminuted form.

The manufacture of cigars has reached a high state of development. Today, even a popular-priced cigar requires the careful blending of as many as fifteen to twenty different types and grades of tobacco. In spite of the great advances which have been made in the design of automatic machines, the making of cigars is still characterized by a large proportion of hand work which limits the rate of production and adds considerably to manufacturing costs. Similar problems arise in the manufacture of cigarettes and pipe tobaccos.

A primary object of this invention is to blend several types and grades of tobacco to a degree of homogeneity heretofore not achieved.

A similar object is to mix tobacco homogeneously with additives, such as flavoring agents, combustion catalysts and adsorbents, in a manner which prevents segregation of the mixed components.

Another important object is to simplify the manufacture of cigars and other smoking products.

Still another important object is to place the manufacture of cigars on a basis more amenable to mechanical operations.

A further object is to curtail the losses of valuable tobacco arising from cutting, stemming, trimming and similar operations practiced in the conventional production of smoking products.

Other objects of the invention will be apparent from the description which follows.

In accordance with this invention, leaf tobacco which has been processed by drying, curing, sweating, fermenting, aging and similar treatments preparatory to its utilization in the manufacture of cigars and like products is comminuted in any of several well-known types of grinders or pulverizers. The tobacco is generally ground to such a degree that all of the particles will pass through a 20-mesh screen and a substantial portion will have a particle size corresponding to the openings of a 40-mesh screen. Considerably coarser and finer tobacco powders are, however, utilizable for the purposes of this invention. The comminuted tobacco is then converted into a plastic mass by thoroughly mixing the dry powder with a limited quantity of a highly viscous

2

aqueous solution of a water-soluble derivative of cellulose.

The quantity of aqueous solution of cellulose derivative which is admixed with the powdered tobacco is limited to that which yields a plastic mass having a consistency approximating that of a good neat cement mortar. An excess of solution detectable by the tendency of the plastic mass to exude liquid should be avoided since any substantial loss of liquid reflects a loss of extractable constituents in the tobacco and consequent alteration of the original smoking qualities of the tobacco. Usually, one part by weight of comminuted tobacco and about two to six parts by weight of the aqueous solution of cellulose derivative will form a paste of the desired consistency.

The plastic mass of tobacco is rolled out into sheets or otherwise pressed or formed into desired shapes, e. g., extruded as a rod or ribbon, and water is then evaporated at moderate temperatures not exceeding about 50° C. from the shaped mass to leave a coherent, self-supporting tobacco product. From the foregoing description, it is obvious that the tobacco has not lost any of its constituents during processing nor has it been subjected to any harmful conditions, such as elevated temperatures or strong acids or bases. Also, comparatively little extraneous matter has entered into the tobacco product. Tobacco processed as hereinabove described is found by tests to have substantially the smoking qualities of the original leaf tobacco. The coherent mass of tobacco particles burns without difficulty and the smoke, judged by experts, has the typical taste and aroma of good quality tobacco.

A very important advantage of the material thus produced is the perfect blending of the various tobaccos used. The homogeneity of the blend results in a correspondingly high uniformity of the products of smoking. In the usual mixing of separate pieces of different tobaccos, such ideal blending cannot be achieved. The smoke which is generated in the combustion of cigars, cigarettes, pipe tobaccos, etc., containing this new tobacco product, represents at all times the result of the simultaneous combustion and dry distillation of all the tobacco types blended, whereas in ordinary smoking products, the heterogeneous distribution of the various tobacco types results in a changing character of the smoke, both in the course of the combustion of a single cigar, cigarette, or charge of pipe tobacco, and from one cigar to another, one cigarette to another, etc., for products of the same basic composition.

Φ00033106Φ

Source: https://www.industrydocuments.ucsf.edu/docs/jmk0000

As used in this specification and the appended claims, the term, water-soluble derivative of cellulose, means any water-soluble derivative of cellulose composed solely of carbon, hydrogen and oxygen atoms. Advantageously such a derivative is of the type represented by the formula:

$$(C_6H_7O_2(OH)_{3-x})_n \cdot (OQ)_{xn}$$

Cellulose radical — Solubilizing radical

showing an ether linkage between the cellulose radical and the solubilizing radical. In the formula, n is a number corresponding to the number of cellulose units in the particular cellulose used, x is a number not greater than 3 depending upon the number of hydroxyl groups in the cellulose unit replaced by ether-linked solubilizing radicals and Q is a radical containing 1 to 4 carbon atoms, preferably 2 carbon atoms. Generally, the more oxygen atoms there are in the radical Q, the better it is for the purposes of this invention; oxygen present in the form of —OH groups is particularly desirable. Representative water-soluble derivatives of cellulose successfully used in this invention are:

Methyl cellulose, $(C_6H_7O_2(OH)_{3-x})_n \cdot (O \cdot CH_3)_{xn}$

Carboxymethyl cellulose,

$$(C_6H_7O_2(OH)_{3-x})_n \cdot (O \cdot CH_2 \cdot COOH)_{xn}$$

Hydroxyethyl cellulose,

$$(C_6H_7O_2(OH)_{3-x})_n \cdot (O \cdot CH_2 \cdot CH_2OH)_{xn}$$

It is well to note that in the production of certain water soluble derivatives, for instance, hydroxyethyl cellulose by the reaction between alkali cellulose and ethylene oxide, the reactant furnishing the solubilizing radical to the cellulose may at the same time undergo polymerization with the result that the cellulose derivative formed may comprise solubilizing radicals which are polymeric in structure. In other words, the radical Q may be composed of a multiplicity of molecular units each containing 1 to 4 carbon atoms in contrast to a single molecular unit, for instance, the single unit $\cdot CH_2 \cdot CH_2OH$ shown above in the formula for hydroxyethyl cellulose. Water-soluble derivatives of cellulose in which the solubilizing radicals have a polymeric structure are useful for the purposes of this invention. Where the water-soluble derivative of cellulose has an acid grouping as in the case of carboxymethyl cellulose, it may be used in the form of the corresponding salt, usually the sodium or potassium salt; the prior statement that the water-soluble derivative of cellulose is composed solely of carbon, hydrogen and oxygen is not intended to exclude the water-soluble salts, e. g., alkali metal salts, of acid-type derivatives of cellulose. At any given temperature and concentration, the viscosity of the aqueous solution of a cellulose derivative will vary with the molecular complexity or weight of its cellulose radical (factor n) as well as with the degree of etherification (factor x). In the foregoing formulae, the factor n is a convenient means used to indicate the polymeric nature of cellulose.

The invention contemplates the use of mixed water-soluble derivatives of cellulose not only in the sense of mixtures of two or more separate and different derivatives but also in the sense of single derivatives having two or more different substituents associated with the cellulose. Thus, in accordance with the first sense, a mixture of equal parts by weight of methyl cellulose and sodium salt of carboxymethyl cellulose may be

employed as the binding agent for tobacco products prepared by the process of this invention. In the other sense, suitable binders are high viscosity grades of single, water-soluble cellulose derivatives having two or more different substituents, which may be exemplified by a cellulose derivative of the type of methyl ethyl cellulose or ethyl hydroxyethyl cellulose. It is well to observe that in a water-soluble cellulose derivative with two or more different substituents not all of the substituents need to be substituents or radicals which exert a solubilizing effect on cellulose when dispersed in water. For example, a mixed cellulose ether might have a relatively small proportion of hexyl radicals serving as one substituent and a relatively large proportion of carboxymethyl radicals serving as the solubilizing substituent. In further connection with the thought that the cellulose need not be heavily substituted to yield a water-soluble derivative adapted for the purpose of this invention, it is interesting to note that the sodium salt of carboxymethyl cellulose used in the examples presented hereinafter is reported to have only 0.4 to 0.6 carboxymethyl group for each anhydroglucose unit of the cellulose molecule or, in other words, for each cellulose radical of the type formula shown hereinbefore.

From the foregoing it is clear that cellulose ethers which are water-soluble and form viscous solutions are particularly useful in this invention. However, the invention is not limited to such ethers and contemplates the use of any suitable water-soluble cellulose derivatives, e. g., cellulose esters made up entirely of carbon, hydrogen and oxygen atoms.

The success of the novel tobacco products of this invention is attributable to the use of cellulose derivatives having several critical properties. An index of suitable water-soluble cellulose derivatives is the viscosity. A suitable cellulose derivative is one yielding a viscosity of at least 1500 centipoises at a temperature of 25° C. when a small quantity thereof not exceeding about 2% by weight is dissolved in water. These cellulose derivatives not only must dissolve in water and yield at low concentrations highly viscous solutions but also must be capable of forming a coherent, tough sheet or mass when their aqueous solutions are evaporated to dryness. The behavior of the cellulose derivative in solution facilitates the preparation of the plastic mass containing the finely divided tobacco as well as the subsequent pressing and shaping of the mass into desired forms. The physical characteristics of the cellulose derivative as deposited from its aqueous solution contribute cohesiveness and flexibility to the tobacco product after it has been dried and conditioned to a desirable moisture content. Accordingly, the product can be easily handled in the manufacture of cigars and other smoking products without encountering any serious crumbling of the product. It will, of course, be appreciated that where some of the product has crumbled because of careless handling, the crumbled material does not represent a loss since it is in a form readily reconvertible to a coherent mass in accordance with the procedure of this invention. Such material may be reworked with water alone or it may be mixed with another batch of comminuted tobacco which is to be processed by my invention; in the latter case, the quantity of cellulose derivative used in the mixture would be adjusted to compensate for the amount in the reworked portion. That properly

0003310 70

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

chosen water-soluble cellulose derivatives should be so effective in producing coherent, self-supporting masses of powdered tobacco is indeed surprising when it is reflected that the finished tobacco product contains less than 20% of the cellulose derivative based on the weight of the tobacco, and frequently less than about 10%. The preferred tobacco compositions contain about 4% to 8% of admixed cellulose derivative based on the weight of the tobacco.

The smoking compatibility of water-soluble cellulose derivatives and tobacco should be safeguarded by the exercise of care in selecting cellulose derivatives in a state of refinement. The refined products should be free of any appreciable quantities of extraneous matter containing compounds of nitrogen, sulfur, phosphorus and the halogens; in short, compounds giving undesirable products of combustion or of dry distillation should be avoided.

It is advantageous to add a small proportion of bentonite or other water-swelling clay to the mixture of tobacco and cellulose derivative. Generally, additions of the order of 1% to 2% by weight of bentonite, based on the weight of dry tobacco powder used, are recommended. It appears that bentonite on swelling in the wet plastic mass of tobacco tends to form a coherent inorganic skeleton or reinforcing network which improves the physical properties of the final product. Tobacco compositions of this invention containing bentonite or like mineral not only are stronger, i. e., show less tendency to crack or crumble, but also exhibit improved smoking characteristics. Moreover, the product burns with a firm, coherent ash. The bentonite tends to adsorb or filter out undesirable tarry constituents and alkaloids of tobacco smoke as it is drawn through the unburned portion of the bentonite-containing tobacco product.

It is often advisable, where the product of this invention is made in sheet form and is later rolled or bent sharply as in making cigars, that the product contain a plasticizer to increase the flexibility and cracking resistance of the sheet. Additions of glycerine of the order of 2% to 15% by weight, based on the weight of dry tobacco used, to mixtures of comminuted tobacco and aqueous solutions of cellulose derivatives with or without bentonite exert an appreciable plasticizing effect. The presence of glycerine in these amounts in the tobacco product does not lead to the formation of unpleasant or troublesome products of complete or incomplete combustion. In the cigarette industry, glycerine is frequently used as a humectant in the tobacco without adverse effects from the viewpoint of smoking. Sorbitol may be substituted for at least part of the plasticizing glycerine.

It is sometimes advantageous to use two or more water-soluble cellulose derivatives in compounding a tobacco product of this invention. Furthermore, water-soluble cellulose derivatives may be successfully used in combination with water-soluble acid polysaccharide compounds, such as sodium alginate, as disclosed in the copending application, Serial No. 677,107, of Walter G. Frankenburg, filed on June 15, 1946, now abandoned.

The water-soluble cellulose derivatives of this invention may also be used in making the highly resilient tobacco sheets or bodies disclosed in another copending application, Serial No. 692,775, of Walter G. Frankenburg, filed on August 24, 1946. The latter application teaches that tobacco sheets or like bodies formed from a paste of comminuted tobacco and a viscous aqueous solution of a suitable binder are more resilient and flexible if fine glass fibers are incorporated in the paste. Fine glass fibers of the order of 0.002" in diameter resembling silk threads not only in appearance but also in softness and flexibility are employed in the proportion of about 1% to 15% based on the weight of the tobacco; preferably, about 2% to 5% by weight of glass fibers are combined with the finely divided tobacco. The glass fibers may be used in the form of loose fibers or in the form of very thin fiber mats. A paste comprising tobacco powder and a viscous aqueous solution of binder may be applied to one or both sides of a thin mat of glass fibers. This invention contemplates the inclusion of glass fibers in the tobacco compositions discussed herein.

In the interests of better understanding and greater clarity, illustrative embodiments of the invention are presented hereinbelow in detail. In these examples, which are not to be construed in any restrictive sense, the proportions mentioned are all based on a common weight unit.

Example 1

Air-dried Pennsylvania leaf tobacco was passed through a Raymond pulverizer operating with a screen of medium-size apertures. The comminuted tobacco comprised a predominant fraction of particles in the size range 20 to 40 mesh. A highly viscous solution (of the order of 50,000 centipoises at 25° C.) was prepared by dissolving 8 parts of the sodium salt of carboxymethyl cellulose (extra high viscosity type) in 375 parts of water; 12 parts of glycerine were mixed with the aqueous viscous solution. The resulting composite liquid was added with stirring and kneading to 100 parts of the pulverized tobacco. The pasty mass obtained by combining the liquid and the tobacco powder had a consistency like that of freshly prepared neat cement mortar and showed no tendency to exude liquid on standing. The pasty mass was placed on plate glass and covered with a sheet of wax paper. With the aid of a roller, the mass was pressed out between the wax paper and plate glass into a layer about 1/60 inch thick. The wax paper was removed and the plastic layer on the plate glass was transferred to a drying chamber in which air at a temperature of 50° C. was circulated. When the moisture content of the tobacco mass had been brought down to about 16%, the product was withdrawn from the drying chamber. The sheet of comminuted tobacco thus produced was self-supporting and fairly pliable. Conditioning of this sheet at 10° C. and at a relative humidity of 90%, increased its plasticity and flexibility considerably. The sheet was put up in the form of small rolls and, in other tests, in the form of irregularly shaped bunches which were then encased with a fine wrapper of Sumatra tobacco. In the cigars thus produced, it is clear that the roll or bunch of sheeted tobacco made in accordance with this invention replaced the filler leaf tobacco and binder leaves conventionally used in cigar manufacture. In blindfold smoking tests, the cigars of this example were not consistently distinguished from ordinary cigars containing the same tobaccos.

Example 2

A viscous solution was prepared by dissolving 7.5 parts of methyl cellulose (4000 cps. type) in

0003310711

Source: https://www.industrydocuments.ucsf.edu/docs/xpmx0000

350 parts of water. To this solution were added 5 parts of glycerine and 3 parts of sorbitol. A blend of American and Turkish tobaccos ground to particles chiefly in the size range of 20 to 40 mesh was mixed with the solution to form a consistent paste; 100 parts of tobacco blend were used. The thoroughly mixed paste was then extruded through a slit 2 inches long and 1/40 inch wide. The extruded ribbon of tobacco paste was deposited on a moving band of wire cloth and dried while on this band by means of a dry air stream at 50° C. After the ribbon of compacted tobacco powder was dried to a moisture content of 19%, it was cut into shreds of the ordinary size used in cigarette manufacture. These shreds were fed into a cigarette machine. The cigarettes made with this material were remarkable for the mildness and aroma of their smoke.

Example 3

A tobacco blend was made by comminuting together 40 parts of Wisconsin binder tobacco, 44 parts of Pennsylvania tobacco and 16 parts of Havana tobacco. The dry powdered mass was mixed with a viscous liquid suspension containing 400 parts of water, 3 parts of the sodium salt of carboxymethyl cellulose (high viscosity type), 3 parts of refined sodium alginate, 10 parts of glycerine and 4 parts of silky glass fibers (length about 1 to 1.5 inch). The resulting paste was pressed out in sheet form and dried in the manner described in Example 1. The finished tobacco sheet showed considerable flexibility and resiliency and passed critical smoking tests.

The invention further contemplates the incorporation, where desired, of additives in the coherent mass of powdered tobacco. Thus, organic substances can be added to the aqueous solutions of cellulose derivatives in order to impart a desirable flavor to the smoke of the resulting tobacco product. In all cases, the incorporation and conservation of the additives is greatly facilitated by the fact that they are imbedded in the bulk of the tobacco mass and are not merely adhering to the surfaces of the leaves, as is the case with additives used with leaf tobacco.

Other valuable additives are ingredients which impart light texture and porosity to the tobacco product. For instance, the addition of diatomaceous earth, advantageously in the proportion of 5% to 10% of the weight of the powdered tobacco, results in a material of relatively high porosity and low density. With some tobaccos, this favors combustion and a high aroma content in the smoke.

The present invention is not to be confused with any suggestions made in prior patents of which a large number issued during the period of 1860 to 1900. These prior proposals generally treated waste tobacco in substantially the same way in which wood, rags, straw, bagasse, etc., are pulped in the manufacture of paper. Some of the later patents acknowledge that the tobacco so converted to paper had lost practically all of the constituents which make tobacco suitable for smoking, and attempted to correct this deficiency by impregnating the tobacco paper with a concentrated decoction obtained by boiling a suspension of tobacco in water. However, all of these earlier schemes failed because it was not appreciated that tobacco and tobacco extracts are inherently delicate and unstable and that even moderate variations in such factors as temperature and hydrogen-ion concentration may adversely effect the tobacco or tobacco extracts by causing decomposition, oxidation, polymerization or other chemical reactions of the compounds in tobacco. In contrast to these prior unsuccessful efforts, the present invention involves the mildest conditions of treatment and avoids the pulping of the tobacco in water or other processing liquid which would extract many soluble tobacco compounds and thus leave an impoverished and deteriorated tobacco product. By way of explanation, the success of the present invention is attributable to the critical selection of water-soluble cellulose derivatives which in aqueous solution are so viscous that substantially no extraction of the tobacco powder occurs during admixture of the powder and viscous solution and which also have the property of binding together the tobacco particles when the admixture is dried.

While the invention is particularly suited for homogeneously blending several tobaccos in a single product, it is still importantly useful in converting even one type or grade of leaf tobacco to a form more uniform in quality and more adapted to mechanical production of cigars and the like. Whether one or several tobaccos are comminuted and made into the products of this invention, the savings in manual labor and tobacco as well as the improvement of smoking properties cannot be overemphasized.

It should be observed that while the products of this invention are made up of comminuted tobacco and a water-soluble cellulose derivative acting as binder, the products may ultimately have the water-soluble cellulose derivative in an insolubilized state because of aging or other natural tendencies or because of special treatments to render the derivative insoluble after the tobacco product has been formed. For instance, a tobacco sheet, prepared by mixing powdered tobacco with a viscous aqueous solution of the sodium salt of carboxymethyl cellulose to yield a consistent paste and by rolling the paste out into a thin layer, might be insolubilized at least in part by contacting the wet layer with a polyvalent metal salt, e. g., a calcium, aluminum or magnesium salt, and by drying the thus treated layer. It is obvious that, after the tobacco product has been compounded and pressed into the desired form, any insolubilization of the water-soluble cellulose derivative used as the binding agent may not be detrimental but rather may be beneficial. Sometimes, metal salts or other substances naturally present in the tobacco may partially insolubilize the water-soluble cellulose derivative which has been compounded with the tobacco to form a tobacco product in accordance with the principles of this invention.

Those skilled in the art will visualize many other modifications and variations of the invention set forth hereinabove without departing from its spirit and scope. Accordingly, the claims should not be interpreted in any restrictive sense other than that imposed by the limitations recited within the claims.

What is claimed is:

1. A tobacco product adapted for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble cellulose derivative having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25% C. when not more than about 2% by weight of said cellulose derivative is dis-

0003310772

Source: https://www.industrydocuments.ucsf.edu/docs/

Feb. 14, 1956 G. P. HUNGERFORD ET AL 2,734,510

TOBACCO SHEET MATERIAL AND METHOD OF FORMING

Filed Aug. 25, 1955 2 Sheets-Sheet 1

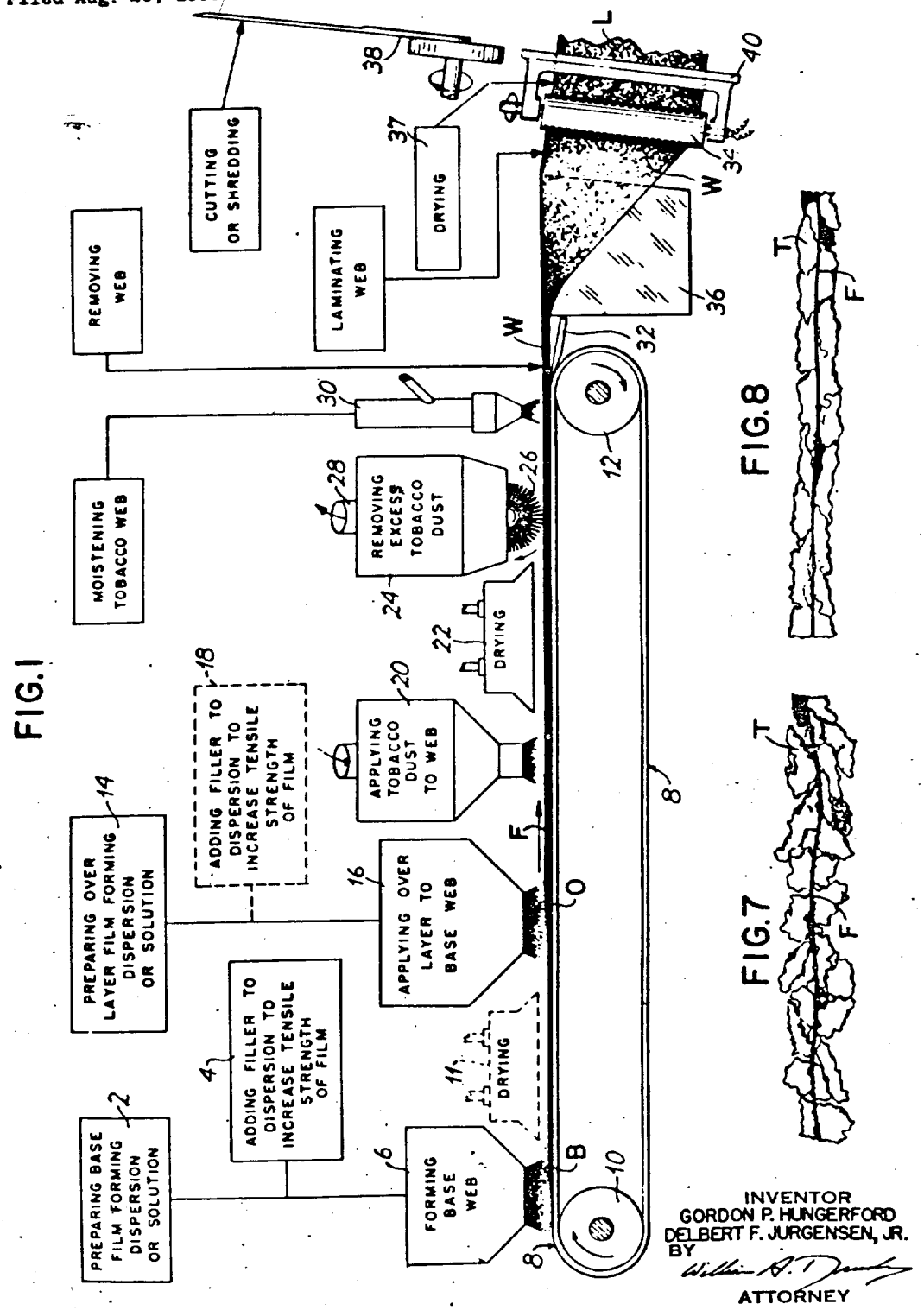


FIG. 1

FIG. 8

FIG. 7

INVENTOR
GORDON P. HUNGERFORD
DELBERT F. JURGENSEN, JR.
BY
William A. Dunlap
ATTORNEY

1002310 73-A

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

solved in water, said cellulose derivative functioning to hold the particles of said tobacco together as a coherent mass.

2. The product of claim 1 wherein the water-soluble cellulose derivative is plasticized by glycerine in an amount corresponding to 2% to 15% by weight of the dry-ground tobacco.

3. The product of claim 1 wherein the water-soluble cellulose derivative is a cellulose ether of the type represented by the formula:

$$(C_6H_7O_2(OH)_{3-x})_n \cdot (OQ)_{xn}$$

wherein Q is a radical containing 1 to 4 carbon atoms, x is a number not greater than 3 and n is a factor indicating the polymeric nature of cellulose.

4. The product of claim 3 wherein the cellulose ether is an alkali metal salt of carboxymethyl cellulose.

5. The product of claim 3 wherein the cellulose ether is methyl cellulose.

6. A tobacco product adapted for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not exceeding about 10% by weight of said tobacco, of a water-soluble cellulose derivative having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight of said cellulose derivative is dissolved in water, said cellulose derivative functioning to hold the particles of said tobacco together as a coherent mass.

7. The product of claim 6 wherein the water-soluble cellulose derivative is an alkali metal salt of carboxymethyl cellulose.

8. The product of claim 7 wherein the alkali metal salt of carboxymethyl cellulose is plasticized by glycerine in an amount corresponding to 2% to 15% by weight of the dry-ground tobacco.

9. The product of claim 6 wherein the water-soluble cellulose derivative is methyl cellulose.

10. The product of claim 9 wherein the methyl cellulose is plasticized by glycerine in an amount corresponding to 2% to 15% by weight of the dry-ground tobacco.

11. A tobacco product in physically continuous and coherent form characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding about 10% by weight of said tobacco, of a water-soluble cellulose derivative having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight of said cellulose derivative is dissolved in water, and a minor proportion, lesser than said minor proportion of cellulose derivative and not exceeding about 5% by weight of said tobacco, of fine flexible glass fibers, said cellulose derivative and said glass fibers holding the particles of said tobacco together in said physically continuous and coherent form.

12. The product of claim 11 wherein the water-soluble cellulose derivative is an alkali metal salt of carboxymethyl cellulose.

13. The product of claim 11 wherein the water-soluble cellulose is methyl cellulose.

14. The improved process of converting tobacco into a physically continuous and coherent form adapted for smoking, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of a water-soluble cellulose derivative in proportions to form a cohesive paste substantially free of exudation, said viscous aqueous solution having a viscosity of at least 1500 centipoises at a temperature of 25° C. and said cellulose derivative yielding a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight thereof is dissolved in water, and shaping and drying said paste into a desired, physically continuous and coherent form adapted for smoking.

15. The process of claim 14 wherein the water-soluble cellulose derivative is an alkali metal salt of carboxymethyl cellulose.

16. The process of claim 14 wherein the water-soluble cellulose derivative is methyl cellulose.

17. The improved process of converting tobacco into a thin sheet adapted for the manufacture of cigars, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of methyl cellulose in proportions to form a cohesive paste substantially free of exudation, said viscous aqueous solution containing not more than about 2% by weight of said cellulose and having a viscosity of at least 1500 centipoises at a temperature of 25° C., and forming and drying said paste into a thin sheet adapted for the manufacture of cigars.

18. The improved process of converting tobacco into a thin sheet adapted for the manufacture of cigars, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of the sodium salt of carboxymethyl cellulose in proportions to form a cohesive paste substantially free of exudation, said viscous aqueous solution containing not more than about 2% by weight of said carboxymethyl cellulose and having a viscosity of at least 1500 centipoises at a temperature of 25° C., and forming and drying said paste into a thin sheet adapted for the manufacture of cigars.

WALTER G. FRANKENBURG.
PAUL W. GARBO.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
21,558	Durell	Sept. 21, 1858
64,591	Stayman	May 7, 1867
2,180,152	Kohler	Nov. 14, 1939
2,307,088	Whiteley	Jan. 5, 1943
2,433,877	Wells et al.	Jan. 6, 1948

FOREIGN PATENTS

Number	Country	Date
879,939	France	Mar. 9, 1943

Source: https://www.industrydocuments.ucsf.edu/docs/xjmk0000

Feb. 14, 1956 G. P. HUNGERFORD ET AL 2,734,510

TOBACCO SHEET MATERIAL AND METHOD OF FORMING

Filed Aug. 25, 1955 2 Sheets-Sheet 2

FIG. 2

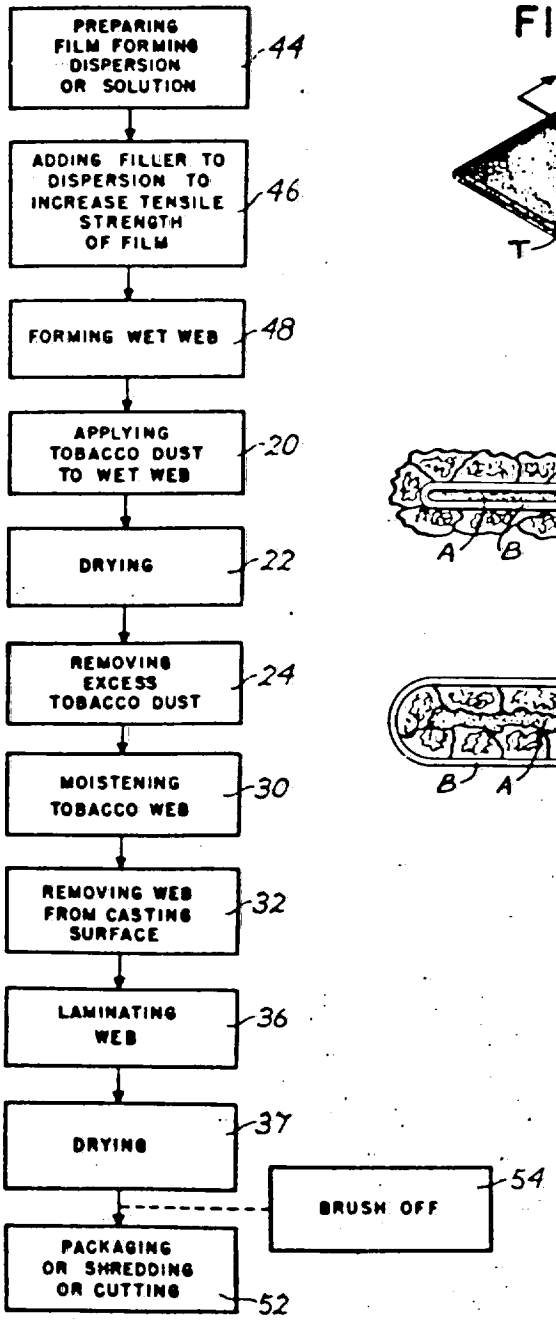


FIG. 3

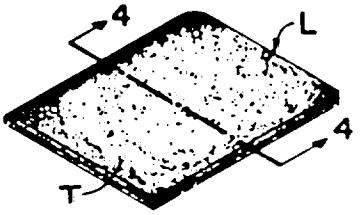


FIG. 4

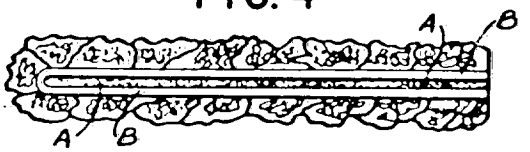


FIG. 5

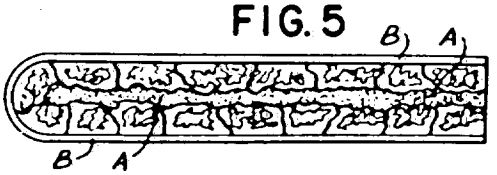
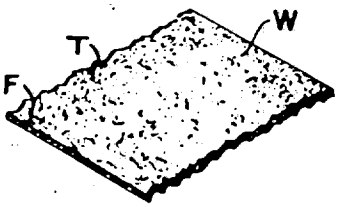


FIG. 6



INVENTOR
GORDON P. HUNGERFORD
DELBERT F. JURGENSEN, JR.
BY
ATTORNEY

Φ0003310 74

Source: https://www.industrydocuments.ucsf.edu/docs/jrbf0000

United States Patent Office

2,734,510
Patented Feb. 14, 1956

2,734,510

TOBACCO SHEET MATERIAL AND METHOD OF FORMING

Gordon P. Hungerford, Westport, Conn., and Delbert F. Jurgensen, Jr., Short Hills, N. J., assignors to American Machine & Foundry Company, a corporation of New Jersey

Application August 25, 1955, Serial No. 530,561

49 Claims. (Cl. 131—15)

This application is a continuation in part of copending application Ser. No. 124,042 filed October 28, 1949, now abandoned.

This invention relates to improved reconstituted tobacco sheets, films, webs, strips and filaments, hereinafter usually referred to as tobacco sheet, or strip material, and to improved methods of producing the same.

The manufacturer of tobacco products generally buys tobacco in the form of whole leaves as removed from the tobacco plant by the farmer. In processing this tobacco, the stem is frequently first removed and then further processing proceeds as desired. In the case of cigarette manufacture, this includes aging, blending, casing and cutting the strip, which is the tobacco laminae remaining after removal of the stem, into shreds and then drying, cooling, screening and forming the shredded tobacco into cigarettes, followed by packaging. In all these operations, which involve much handling of the tobacco, waste fines and dust are formed. At the present time these waste materials, stems, field scrap (farm damaged leaves), fines and dust have essentially no value to the tobacco manufacturer, and are sold to manufacturers of fertilizers, and insecticides at a fraction of a cent per pound. Much of this waste tobacco material is of good quality from a smoking standpoint. Indeed it is believed that this waste tobacco material contains a disproportionately high percentage of the very best quality smoking tobacco, since the latter comprises the thinnest, lightest, most friable leaves which would most readily break up into fines and dust on handling. These high quality fines are useless now only because of their physical form. A technique for processing this good tobacco into a form which would render it usuable in smoking articles without essential change in its smoking characteristics would therefore be attractive to a tobacco manufacturer since it would tend to reduce manufacturing costs.

It has been suggested previously that reconstituted tobacco strip material be made by wet milling a mixture of tobacco in water to form therefrom a slurry which can be converted, as by any well-known casting and drying method, into continuous self-supporting sheets and strip material.

Other attempts to solve the problem of forming a satisfactory reconstituted tobacco sheet material could be cited, such as by forming tobacco paper using well-known paper-making techniques, and also by forming calendered tobacco impregnated films. However, despite these attempts, little success has been achieved and to our knowledge, none of these processes has ever been used commercially.

The present invention constitutes a solution to the problem of reconstituting tobacco materials by converting them into reconstituted tobacco sheet or strip material which can be used in the same manner as natural leaf tobacco in tobacco products such as cigarettes, cigars and the like. Tobacco sheet or strip material made in accordance with our invention is elastic, flexible, tough, self-supporting and continuous, and possesses dry and wet strengths comparable to that of natural leaves or pieces of tobacco, and retains substantially all natural characteristics and properties of tobacco, including color, aroma, and taste on smoking. This is necessarily true since in our process, the waste tobacco is merely dry ground, then deposited onto the top surface of a film-forming material. Thus the principal portion of the tobacco does not contact water or other foreign processing material, nor is its basic physical form (a natural, fibrous, somewhat porous, cellular structure) destroyed by the grinding or milling which is characteristic of previously suggested procedures. Therefore, this process, unlike many that have been previously proposed for utilization of waste tobacco materials, would allow the utilization of such tobacco materials without change from the natural chemical condition in which they exist in normal smoking products. This constitutes an important advantage of our process.

It is an object of our invention to provide an improved method of making novel reconstituted tobacco sheet or strip material in which a continuous wet web is formed from a film-forming material to which finely ground tobacco is applied so that the ground tobacco material adheres to the film-forming material in the wet web, and forms an integral part of the web of reconstituted tobacco material produced.

It is a further object of our invention to provide an improved method of making novel reconstituted tobacco sheet or strip material involving the formation of a base layer of a film-forming material and applying thereto an overlayer of a film-forming material, and while the latter is in wet condition, applying, as by blowing, finely ground particles of tobacco to the top thereof, such that the ground tobacco particles adhere thereto, the resulting product having characteristics similar to those of natural tobacco.

The invention also consists in the provision of an improved method of reconstituting tobacco by forming a wet layer of a film-forming material on a base web of similar film-forming material and then applying, as by blowing, finely ground particles of tobacco to said wet web, after which the web is dried, treated as by brushing, to remove excess tobacco, laminated and preferably treated by heated rollers to compact the outwardly projecting tobacco particles to form a porous, reconstituted tobacco sheet or strip material which can be made into filaments by shredding, or cut into sheets or strips for use in making smoking articles such as cigarettes, cigars and the like.

With these and other objects not specifically mentioned in view, the invention consists in certain features which will be hereinafter fully described, and then set forth in the claims hereunto appended.

In the accompanying drawings, which form a part of this specification, and wherein the several reference characters designate the same or like elements:

Figure 1 is a diagrammatic, schematic illustration disclosing the preferred method of performing the invention;

Figure 2 is a view showing diagrammatically a modified method of producing our novel reconstituted tobacco sheet material;

Figure 3 illustrates a piece of the laminated reconstituted tobacco produced by our method;

Figure 4 is a sectional view, greatly enlarged, taken on line 4—4 of Figure 3;

Figure 5 is a cross-sectional view, greatly enlarged, of a modified type of our novel reconstituted tobacco sheet or strip material in which the tobacco-covered surfaces of the film are adhered to each other;

Figure 6 is a view showing a single thickness of our novel reconstituted sheet material;

Figure 7 is a diagrammatic, cross-sectional view of a highly magnified piece of our novel reconstituted tobacco material not heat-pressed; and

Φ00331075

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Figure 8 is a view, similar to Figure 7, showing the material after being heat-pressed.

Referring to the drawings, in Figure 1, which shows diagrammatically the steps covering the preferred method of our invention, 2 designates the step of preparing a dispersion or solution of a film-forming material used in making the base web of our reconstituted tobacco sheet. Any film-forming material can be used which possesses adequate strength, retains the tobacco particles well, and which, on smoking the final reconstituted tobacco film, does not cause an unsatisfactory taste, aroma or harshness in the smoke. Stated otherwise, the film-forming material used does not introduce disagreeable flavors or aromas into tobacco smoke. Hence its presence is not objectionable to smokers or users of the product. Suitable film-forming materials are soluble salts of carboxymethylcellulose and carboxymethyl hydroxyethyl cellulose, or carboxymethylcellulose and carboxymethyl hydroxyethyl cellulose, the latter two being insoluble in water, but, as described hereinafter, capable of being formed into stable water dispersions in the manner described in a copending application filed by Newton Heimbach on December 21, 1949, for Water Insoluble Coatings, Films and Adhesives and Method of Making Same, Serial No. 130,858. These dispersions are capable of being cast to form a wet web which when dried, becomes a self-supporting film. The terms "carboxymethylcellulose" and "carboxymethyl hydroxyethyl cellulose" where used herein, mean the free acid form of these compounds.

While the strength of films formed from the above-mentioned types of dispersions or solutions is high, it is preferred to add a small quantity of an inert and tasteless filler to the dispersion or solution before forming into the wet web or filament to increase the tensile strength of the product (as indicated at 4 in Figure 1). Materials such as kaolin and fuller's earth have produced satisfactory results. Finely ground tobacco waste may also be used for this same purpose. Also, strengthening and/or waterproofing materials, such as glyoxal, which presumably react with the film-forming constituent to modify the type of intermolecular or intermicellar linkages, can be added, if desired, to the above-mentioned solutions and dispersions. When a filler and/or additive is used, it is mixed with the film-forming solution or dispersion, after which the dispersion is converted in any suitable manner as by coating or spraying upon a film-forming surface, into a continuous layer or wet web and dried as desired to form continuous self-supporting dry sheets or strips, as the case may be.

As indicated in Figure 1, the film-forming dispersion or solution is applied, as by spraying, by a suitable device 6 upon the surface of an endless traveling belt 8 to form a continuous wet web, which in the preferred method, is termed the base web B. If desired, small sized individual sheets can be cast directly at spaced intervals on belt 8 or on flat plates (not shown). Belt 8, or plates (not shown) upon which film B is cast or formed in any other suitable manner, are best made of a material which will not react noticeably with the film-forming material to cause discolorations, spots or marks. Suitable materials for this purpose are stainless steel, or chromium-plated belts or flat endless bands, or flat plates of the same materials or similarly treated materials.

Belt 8 runs on driven and driving pulleys 10, 12, preferably continuously driven in order that the web may be moved by the upper lap of the conveyor belt past the several stations necessary to complete the operations of the method. Following the casting of base web B on belt 8, the moving belt carries the wet base web B through a drying station indicated generally at 11, after which an overlayer O is applied to the upper surface of the base web B. While it is desirable to dry base web B before the application of overlayer O thereto, this step may be omitted and satisfactory results will be obtained.

Overlayer O is prepared in the same general manner as base web B. That is, an aqueous solution of sodium carboxymethylcellulose or aqueous dispersion of carboxymethylcellulose, or other suitable film-forming, adhesive material, which will bond to both the base web and the tobacco particles, is prepared, as at 14, and applied by a suitable applying device 16 to base web B. If desired, a filler such as kaolin can be admixed as at 18 with the overlayer adhesive solution or dispersion prior to its application to the surface of base layer B. Also, strengthening and/or waterproofing materials, such as glyoxal, which presumably react with the film-forming constituent to modify the type of intermolecular or intermicellar linkages, can be added, if desired, to the above-mentioned solutions and dispersions. The base layer B and overlayer O are substantially equal in width and extend approximately to the longitudinal edges of endless band 8, although obviously the web width can be varied as desired. It is usually preferred that the solution or dispersion used in forming overlayer O be less viscous than that used in making base web B. It is advantageous to make the base web of high concentration to minimize the amount of drying required at 11 and advantageous to make the overlayer comparatively fluid to obtain maximum strength of bond between the tobacco particles and the film-forming base web.

It has been found that satisfactory reconstituted tobacco sheet or web material, made in accordance with our invention, is formed when the base web and overlayer web are formed of a solution of sodium carboxymethylcellulose, or an aqueous dispersion of carboxymethylcellulose. A satisfactory product is also produced when the base web is made of a solution of a soluble carboxymethylcellulose salt and the overlayer web is formed from an aqueous dispersion of carboxymethylcellulose, or vice versa. It is, however, preferred to use carboxymethylcellulose for both layers B and O because the final product then exhibits greater resistance to the steam and moisture used in "casing" tobacco in the tobacco factory and to the saliva in the smoker's mouth.

Following the application of overlayer O to base web B, the wet composite web on conveyor 8 moves to a tobacco dust applying station 20, where mechanism of suitable design applies tobacco dust to the entire surface of the wet web moving therethrough. The term "dust" as used herein is intended to mean ground or finely divided tobacco. It may be formed from tobacco of any suitable type, as for instance, whole leaves or portions thereof, stems, or waste tobacco including field scrap, or clippings, dust, siftings and chips resulting from the manufacture of cigarettes, cigars and other tobacco products, or from whole tobacco plants including stalks and whole leaves attached thereto. In preparing this "dust," it is believed preferable to separate and remove foreign material such as sand and dirt which oftentimes is mixed with tobacco. The latter is then dry ground to a suitable particle size. We have found that satisfactory results are obtained when the particles are 7 microns minimum size, 600 microns maximum size, and average between 100–150 microns, although this is not critical, and depends upon the characteristics desired in the finished product.

A suitable device for applying tobacco dust to the surface of web O is a blower connected by a conduit to a nozzle, the latter being moved back and forth across the moving wet web O as the air blast forces tobacco dust from the nozzle into adhering relationship with the web, whereby substantial quantities of dust adhere thereto.

In the application of tobacco dust to the wet composite web consisting of base film B and overlayer film O, an excess of dust is usually applied, as by blowing at overlayer O, in order that wet overlayer film O will be thoroughly coated.

The quantity of tobacco dust per unit area of product

Φ00033107G

Source: https://www.industrydocuments.ucsf.edu/docs/xjmf0000

can be varied by changing the air velocity, quantity of dust blown onto wet web O, viscosity of web O, its thickness, and the particle size of the tobacco dust, to obtain the product desired. In a typical case, when the wet web O is 10 mils (ten one-thousandths of an inch) thick and its viscosity is 800 centipoises, and a great excess of tobacco dust is blown upon the wet web O at 7000 ft. per minute air velocity, tobacco loadings up to 8–12 grams per square foot have been obtained. The ratio of dust applied to the surface of web O, as by blowing, to dust adherence to web O, varies depending upon the dust loading desired. If light loading of dust is desired, a small quantity of dust per unit area of web is applied and a large percentage adheres to the wet web. When striving for heavy loading of web O, larger quantities of dust per unit area are applied to the web relative to the amount that adheres thereto. In operation, we adjust the quantity of dust applied or blown upon the web until a desired loading is obtained, or until a maximum loading is obtained.

It is noted that because of the excellent tensile strength of our web, it is possible to load the web with tobacco dust until the final tobacco sheet or strip material produced is very predominantly tobacco. However, tobacco sheet made according to this invention may range in composition from 50 per cent or more of binder material to as little as 4 per cent or less binder material on a dry basis where the remainder of the sheet is tobacco material. Preferred tobacco sheet, made according to this invention, ranges in composition between twice as much tobacco as adhesive film on a dry weight basis per unit area and twenty times as much tobacco as adhesive film on a dry weight basis per unit area. We have made satisfactory reconstituted tobacco sheet or strip material in accordance with the invention with a loading of 85 parts of tobacco by weight in the finished material to 15 parts by weight of film or web forming material, including fillers and/or humectants. It is possible to increase the tobacco loading still further depending upon the desired tensile strength, thickness of film, plasticity, and other characteristics desired in the final reconstituted tobacco sheet material. In short, our product is mainly tobacco held together by a relatively thin, light-weight, web or net of high tensile strength film or web-forming material, which on smoking, has substantially no objectionable or deleterious sensory reaction to a smoker. Dust which does not adhere to the wet web is recovered from the air stream in which it is blown upon the web, and reused.

From what has been said above and as noted hereinafter, the heavy tobacco loading is well in excess of five times the weight of the film per unit area. As noted above, tobacco loadings up to 8–12 grams per square foot have been obtained in the final product. Where, as shown in Example 6 given hereinbelow, which describes an example of our reconstituted tobacco material, the weight of the film which is loaded with the tobacco dust and fine particles is 1.3 grams per square foot, it is readily apparent that the tobacco loading ranges between 6.15 and 9.23 grams per square foot.

As shown in Figure 1, moisture can be removed from tobacco coated web O by any known suitable moisture extracting device 22, after which the tobacco covered composite web W, shown in exaggerated thickness in Figure 1, consisting of base layer B, overlayer web O and the layer of tobacco dust adhering to overlayer O, is subjected to the operation of removing excess, loosely adhering tobacco dust from the surface of web W. This is effected by means of any suitable device 24, such for example as transversely extending rotary brush 26 mounted in operative relationship with a suction exhaust 28. The dust thus removed may be recovered by any suitable known means and reused. The brushed, continuous tobacco sheet or strip material is then subjected to a moistening operation which is advantageous to the satisfactory removal of the sheet or strip W from conveyor 8. As shown, any known type of moistening device can be used, such as a spray or atomizing device which will spray water in a mist upon the upper surface of the sheet or strip W. The moisture content of the sheet or strip W is thus raised to facilitate its removal from belt 8, as by a doctor blade 32. We have found that a moisture content of approximately 30% gives good results. This can be varied widely, however, depending upon thickness of film, tobacco loading, and method of removing the sheet or strip W from the belt.

Upon removal of the sheet or strip W from conveyor 8, the conveyor belt side of the sheet may be coated with a parting agent such as ground tobacco or talc to prevent sticking. The sheet may then be passed between heated or unheated pressure rollers, if desired, to increase the apparent density of the product. The sheet or strip is then dried as at 37 to the desired final moisture content, e. g. 10–12%, after which it may be reeled into rolls, or cut into sheets, sections or shreds as desired. Obviously the order in which these operations is carried out is not critical. For example, the moist sheet might be first cut into sections and then dried.

It is, however, preferred to form a laminated tobacco sheet or strip material structure. This effectively prevents any tendency of films or sheets to stick together when reeled or stacked and also results in stronger films. One way of laminating the sheet or strip W is indicated in Figure 1. This includes feeding sheet or strip material W by any suitable web feeding means, such as coacting rollers 34, over a stationary plow member 36, whereupon sheet or strip material W is folded longitudinally into two continuous sections which are brought into back to back relationship, and due to the adhering qualities of base film B, unite under the pressure of rollers 34 and form a laminated film or web L. Sheet or strip material W can also be laminated by bringing two strips of continuous film into back to back relationship and pressing them together as by rollers 34. This produces a laminated sheet or strip material having the general appearance shown in Figure 7, and in greatly enlarged detail in Figures 3 and 4. Rollers 34 may be heated or very high pressures may be used with a comparatively moist sheet so that as the two sheets or strips are being pressed together, the sections thereof or portions are not only joined firmly together, but also particles of tobacco projecting upwardly beyond the plane of the face of the web film, are compacted and pressed downwardly into more or less contiguous relationship, but not forced to any significant extent into the film. Figure 8 shows the sheet or strip after such pressing. By this technique, it is believed possible to control the burning of the product to some extent, since by hot pressing, or by high-pressure pressing while moist, the apparent density of the product may be somewhat increased, tending to result in possibly slightly more distillation of tars and resins (less complete combustion) when the product is smoked. Also, the pressed product exhibits a superior adherence of the tobacco dust to the surface of the sheet. The product being smoother surfaced, it is less likely to lose dust in handling and it exhibits a more natural tobacco-like feel between the fingertips.

In the above discussion, reference is made to the optional step of hot pressing. The temperature must not be sufficiently high to change or alter the tobacco constituents in any deleterious way. Temperatures of approximately 180° F. in combination with relatively high pressures and short contact time, have been found effective. Similar results have been obtained at lower temperatures with comparatively higher pressures and higher moisture contents in the sheet. It should be noted that such pressing of the finished sheet does not result in a non-porous, high density product as would be obtained by calendering the wet stock before drying. It is thought that such a product would be inferior in taste on smok-

US00033107A

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

ing because of excessive distillation and incomplete combustion resulting from its lack of porosity.

In Figure 5, a modified type of sheet or strip material L is shown in which the tobacco-coated surfaces of the reconstituted sheet, web or film material are treated with a small quantity of suitable adhesive A, such as the material used in making webs B and O, and then brought into juxtaposition and pressed, as described above, into adhering relationship. This gives a stronger product having smooth surfaces. It is sometimes helpful to dust the exposed surfaces of the so laminated sheet with talc or tobacco dust or other suitable material to prevent "blocking" (sticking together under pressure).

After being laminated, sheet or strip material L is moved to a dryer where the moisture content is reduced to any desired figure, e. g. 12%. At times it may then be advantageous to again brush the sheet to remove loosely adhering tobacco particles. The sheet or strip material L is then moved to a cutting device consisting of a rotating blade 38 and ledger blade 40, which cuts sheet or strip material L into desired lengths. If desired, however, laminated sheet or strip material L may be rolled into a reel (not shown), or it can be shredded by any suitable shredding device, such for example as that indicated in Rundell Patent 2,184,567 issued December 26, 1939.

Examples of typical film-forming solutions and dispersions are given as follows:

EXAMPLE 1

Sodium carboxymethylcellulose solution

Composition of base web:	Percent by weight
Sodium carboxymethylcellulose (high viscosity)	1.5
Kaolin	0.75
Glycerine	1.5
Water	96.25

EXAMPLE 2

Sodium carboxymethylcellulose solution

Composition of overlayer:	Percent by weight
Sodium carboxymethylcellulose (high viscosity)	1.0
Kaolin	0.5
Glycerine	1.0
Water	97.5

We have found that satisfactory results are obtained using high viscosity sodium carboxymethylcellulose (sodium cellulose glycolate) in concentrations between 1 and 8% by weight in water. In the case of the overlayer web, the concentration is usually lower than 8% by weight. Obviously low viscosity and medium viscosity sodium carboxymethylcellulose (sodium cellulose glycolate) in suitable concentrations may be used if desired but give less advantageous results.

In the above examples, the constituents are added in any order and mixed thoroughly. If kaolin is added, it is necessary to use a colloid mill or other known type of dispersing apparatus to disperse the kaolin uniformly.

As noted above, and in all other examples, it is preferrred to use a humectant and/or plasticizer such as glycerine which tends to prevent the final reconstituted tobacco sheet or web material from becoming too dry and brittle. In the examples given herein, the sodium salt of carboxymethylcellulose is used. However, if desired, other soluble carboxymethylcellulose salts, such as the potassium and ammonium salts, can be used.

EXAMPLES 3 AND 4

Acid carboxymethylcellulose dispersions

Percentages of materials used are the same as in Examples 1 and 2, except that carboxymethylcellulose (cellulose glycolic acid) is used as the film forming ingredient instead of sodium carboxymethylcellulose.

Typical dispersions can be prepared as follows: A 1/16 inch diameter stream of a 3.75 per cent high viscosity sodium carboxymethylcellulose solution in water is extruded into about twice its weigth of 20 per cent sulfuric acid. The sodium carboxymethylcellulose solution forms threads which are allowed to stand in the acid two hours to complete the acidification of the sodium carboxymethlcellulose. The threads of reacted carboxymethylcellulose are then removed from the acid by means of a suitable screen. The insoluble carboxymethylcellulose is then washed with a stream of water until the pH of a dispersion formed by processing a sample of the carboxymethylcellulose threads in a "Waring" blender is 2.4. At this point, the washing may be discontinued. The carboxymethylcellulose, which is now in the form of semi-solid, long, gelatinous strands, is then ground in a colloid mill, "Waring" blender, or similar device to produce a fine dispersion of carboxymethylcellulose in water.

The following conditions have been used to produce a satisfactory carboxymethylcellulose dispersion:

Conditions	Example 3	Example 4
Orifice diameter (Inches) (through which sodium carboxymethylcellulose solution is extruded into acid)	1/16	1/4
Concentration of sodium carboxymethylcellulose solution (wt. percent)	3.75	3.75
Weight of sodium carboxymethylcellulose solution (lbs.)	70	70
Concentration of H_2SO_4 solution (wt. percent)	20	20
Weight of H_2SO_4 solution (lbs.)	135	135
Acidification time (hours)	2	8
Washing time (hours) (water rate about 6 gals./min.)	1/2	3 1/2
pH of carboxymethylcellulose dispersion after washing and dispersing in colloid mill	2.4	2.4

To make a dispersion suitable for casting, the concentrated carboxymethylcellulose, prepared as described above, may be diluted to the desired concentration by the addition of water, the desired quantities of kaolin and glycerine added, and if desired, glyoxal may also be added, and the mixture dispersed in a colloid mill or other suitable device.

In forming satisfactory aqueous carboxymethylcellulose dispersions, it is found that good results are obtained when the concentration of the sodium salt of carboxymethylcellulose solution ranges between 2 and 8% by weight, and the final sulfuric acid concentration is between 5 and 25%. The time of acidification may vary over wide limits, as may the washing time. The pH of the final carboxymethylcellulose dispersion may also vary from about 1.5 to 5.0. Satisfactory results have been obtained using kaolin between 0 and 8% by weight, and glycerine ranging between 0 and 10% by weight based on the total weight of dispersion. When glyoxal is used, good results are obtained when the weight of glyoxal is between 0 and 20% of the weight of soluble cellulose glycolate salt or cellulose glycolic acid contained in the solution or dispersion.

The techniques described hereinabove for forming aqueous dispersions of cellulose glycolic acid are following in making aqueous dispersions of carboxymethyl hydroxyethyl cellulose which for our purpose has characteristics similar to those of cellulose glycolic acid. A satisfactory dispersion of acid carboxymethyl hydroxyethyl cellulose for use in forming sheet or strip material was made as follows:

EXAMPLE 5

Four and one-tenth grams of sodium salt of carboxymethyl hydroxyethyl cellulose were dissolved in water to form a thick paste. The paste was extruded through a 1/16 inch diameter orifice into 20% sulfuric acid and was permitted to stand in the acid for two hours. The

0003310078

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

hardened spaghetti-like threads of the insoluble acid form of carboxymethyl hydroxyethyl cellulose were removed from the acid, drained and washed with running water for twenty minutes. The washed threads were then dispersed in a manner similar to that described in Examples 3 and 4 to form an aqueous dispersion which was formed into a wet web which was coated with tobacco dust and dried to form a continuous reconstituted tobacco sheet and strip material.

In forming the webs decribed hereinabove, the solutions or dispersions can be applied to belt 8 by spraying, spreading with a casting knife, such as that described in co-pending Jurgensen and Hungerford application, Serial No. 49,968, filed September 18, 1948, for Film Casting Knife and Process, now U. S. Patent 2,546,342, issued March 27, 1951, or by other known web or film-forming devices. The amount of dispersion generally applied or cast upon belt 8 depends upon the strength desired in the final product, and the concentration and the composition of the dispersion. The quantity of film-forming material in overlayer O must be sufficient to secure the tobacco to the base web, and the thickness of web B must be sufficient to provide the strength desired.

Typical examples of base web, overlay and tobacco quantities are as follows:

EXAMPLE 6

Base web material	Example 1.
Thickness of base web (wet) in 1/1000 inch	8.
Overlay material	Example 2.
Thickness of overlay (wet) in 1/1000 inch	10.
Weight of reconstituted tobacco web material (gms./ft.^{2}) (dry).	8.
Weight of web, including fillers and humectants (gms./ft.^{2}), (dry) (not including tobacco).	1.3.

Figures 3 and 4 illustrate pieces or sheets of laminated reconstituted tobacco sheet or strip material L produced by our method. In Figures 3 and 4, and also in Figures 5 to 8 inclusive, T designates the tobacco dust and fine particles, and F indicates the tobacco-loaded continuous supporting film.

Figure 2 discloses a modified method which is generally similar to the method disclosed in Figure 1, except that it omits the formation of an overlayer web. As disclosed in Figure 2, any suitable film-forming dispersion or solution is prepared. This may be made from a water-soluble salt or carboxymethylcellulose or from carboxymethylcellulose in the manner described above in connection with the preferred method illustrated in Figure 1. To the prepared film-forming dispersion or solution is added, as at 46, a quantity of filler such as kaolin or fuller's earth which, as described above, increases the tensile strength of the film. Also, other strengthening and/or water-proofing additives such as glyoxal may be used. While the addition of a filler is desirable, it can be omitted since it is not essential to the production of a satisfactory reconstituted tobacco sheet material. After the filler has been admixed with the prepared film-forming dispersion or solution, the latter is formed into a wet web as at 48 on an endless conveyor belt 8 in the manner disclosed in Figure 1. An excess of tobacco dust is applied at 20 to the surface of the wet web and moisture is then removed therefrom by means of a suitable drying device indicated at 22. Following this operation, loosely adhering tobacco dust is removed by means of a suitable device designated 24. The resulting sheet or strip material W is then moistened as at 30, removed from conveyor 8 by a doctor blade 32, laminated as at 36, dried and then shredded or cut for packaging or manufacture into smoking articles as indicated at 52. In some cases, it may be desirable to again subject the laminated sheet or strip material to the action of a brushing or dust-removing device such as 54 after the removal of the laminated sheet or strip material from conveyor 8 and drying if for any reason tobacco particles have been loosened from the sheet or strip. This operation is not necessary, but in some cases has proven desirable. As noted above, single layer sheets can be produced by omitting the step of lamination. If desired, the product may be pressed, as disclosed above.

If desired, in the methods described above, tobacco dust can be applied to the undersurface (film side) of the reconstituted tobacco sheet or strip material W upon its removal from conveyor belt 8. If this is done, the underside of sheet or strip material W is moistened or coated with an adhesive, such as a light spray of the overlayer composition such as described in Example 2 or 4. An excess of tobacco dust is then applied to the wet undersurface of sheet or strip material W. The composite sheet or strip material resulting therefrom is then dried, excess tobacco is removed and a reconstituted tobacco sheet material or strip material designated W^1 having a tobacco coating on both sides, such as shown in Figure 6, is produced. Sheet or strip material W^1, if desired, can be pressed to compact the projecting tobacco particles and produce a sheet or strip having the general appearance of the sheet shown in Figure 8, except that it contains but a single layer of film-forming material.

If desired, narrow reconstituted tobacco filaments can be made by applying the above-described film-forming dispersions to the surface of endless traveling conveyor 8 by suitable casting or extruding mechanism, which can be similar to that disclosed in Wells et al. Patent 2,433,877, issued January 6, 1948, after which the filaments are coated with tobacco in the same manner as the webs or films formed in accordance with the methods disclosed in Figures 1 and 2.

While preferred embodiments of the invention have been shown and described, it is to be understood that the invention is not confined to the specific method steps and the details of construction of the apparatus for carrying out the methods herein set forth, by way of illustration, as it is apparent that many changes and variations may be made therein, by those skilled in the art, without departing from the spirit of the invention, or exceeding the scope of the appended claims.

What is claimed is:

0000331079

1. Tobacco sheet material comprising an initially water insoluble water dispersed adhesive material and finely divided tobacco the principal portion of which is dry ground when associated with said adhesive material.

2. Tobacco sheet material comprising a water insoluble layer of film forming material and a coating of finely divided tobacco covering and adhering to the surface of said layer in excess of five times the weight of said film forming material on a dry basis per unit area.

3. Tobacco sheet material comprising a water insoluble layer of film forming material and a coating of finely divided tobacco covering and adhering to the surface of said layer in excess of two and less than twenty times the weight of said film forming material on a dry basis per unit area.

4. Tobacco sheet material comprising a water insoluble layer of film forming material and a coating of finely divided tobacco adhering to one surface or side of said layer of film forming material in excess of two and less than twenty times the weight of said layer of film forming material on a dry basis per unit area.

5. Tobacco sheet material comprising a water insoluble layer of film forming material and a coating of finely divided tobacco adhering to both surfaces or sides of said layer of film forming material in excess of two and less than twenty times the weight of said layer of film forming material on a dry basis per unit area.

6. Tobacco sheet material comprising a tobacco free layer of film forming material and a coating of finely divided tobacco covering adhering to the surface of said layer in excess of five times the weight of said film forming material on a dry basis per unit area.

7. Tobacco sheet material comprising a tobacco free

Source: https://www.industrydocuments.ucsf.edu/docs/xjnw0000

layer of film forming material and a coating of finely divided tobacco covering and adhering to the surface of said layer in excess of two and less than twenty times the weight of said film forming material on a dry basis per unit area.

8. Tobacco sheet material comprising a tobacco free layer of film forming material and a coating of finely divided tobacco adhering to one surface or side of said layer of film forming material in excess of two and less than twenty times the weight of said layer of film forming material on a dry basis per unit area.

9. Tobacco sheet material comprising a tobacco free layer of film forming material and a coating of finely divided tobacco adhering to both surfaces or sides of said layer of film forming material in excess of two and less than twenty times the weight of said layer of film forming material on a dry basis per unit area.

10. Tobacco sheet material comprising a base web of tobacco free film forming material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, and water soluble salts of carboxymethyl hydroxyethyl cellulose, an overlayer of a similar material covering the surface of said base web and forming therewith a composite web, and finely divided tobacco covering and adhering to said overlayer of said web.

11. Tobacco sheet material comprising a continuous self supporting web containing a film forming material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose and water soluble salts of carboxymethyl hydroxyethyl cellulose, and tobacco dust covering and intimately adhering to the surface of said film in excess of five times the weight of said film forming material on a dry basis per unit area.

12. Tobacco sheet material comprising a continuous self supporting web containing a film forming material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose and water soluble salts of carboxymethyl hydroxyethyl cellulose, and tobacco dust covering and intimately adhering to the surface of said film in excess of two and less than twenty times the weight of said film forming material on a dry basis per unit area.

13. Tobacco sheet material comprising a film of cellulose derivative film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, and tobacco dust covering and adhering to both surfaces of said film in excess of five times the weight of said film on a dry basis per unit area.

14. Tobacco sheet material comprising a film of cellulose derivative film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, and tobacco dust covering and adhering to both surfaces of said film in excess of two and less than twenty times the weight of said film on a dry basis per unit area.

15. Tobacco sheet material comprising two continuous tobacco free webs of film forming material adhered together, said film forming material being selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, and a coating of finely divided tobacco over the outer surface of each of said webs.

16. Tobacco sheet material comprising a web of film forming material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose and water soluble salts of carboxymethyl hydroxyethyl cellulose, an overlayer web of said forming material adhering to said base web and a substantially uniform coating of tobacco dust adhering to the surface of said overlayer web.

17. Tobacco sheet material comprising a composite sheet including a layer of tobacco free material selected from the group consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, and a layer of finely divided tobacco adhering to the surface of said tobacco free material.

18. Tobacco sheet material comprising a composite film consisting of cellulose glycolic acid and substantially uniformly distributed finely divided tobacco adhering to said film and forming an integral part thereof.

19. Tobacco sheet material comprising a composite sheet consisting of a thin substantially water insoluble film of carboxymethyl hydroxyethyl cellulose, and finely divided tobacco particles adhering to and substantially uniformly covering the surface of said film.

20. Tobacco sheet material comprising a film of carboxymethyl cellulose, and tobacco dust in a quantity at least five times the weight of said film of carboxymethyl cellulose per unit area, the tobacco dust constituting a covering adhering to said film.

21. Tobacco sheet material comprising a film of carboxymethyl cellulose, and tobacco dust in a quantity at least two and less than twenty times the weight of said film of carboxymethyl cellulose per unit area, the tobacco dust constituting a covering adhering to said film.

22. Tobacco sheet material comprising two continuous lengths of film consisting of carboxymethyl cellulose, each of said lengths of film having a coating of tobacco dust substantially uniformly covering one surface thereof, the uncoated surfaces of said films being adhered together and forming a laminated web construction.

23. Tobacco sheet material comprising a continuous tobacco free film of a water soluble salt of cellulose glycolic acid and a coating of finely dvided tobacco covering the surface of said film and adhering thereto.

24. Tobacco sheet material comprising a continuous tobacco free film of a water soluble salt of carboxymethyl hydroxyethyl cellulose and a coating of finely divided tobacco covering the surface of said film and adhering thereto.

25. A method of forming tobacco sheet material which comprises contacting an initially water insoluble adhesive material dispersed in water with finely divided tobacco the principal portion of which is dry ground.

26. The method of making tobacco sheet material comprising preparing a dispersion of a film forming material which becomes substantially water insoluble when dry, adding a small quantity of a film strengthening filler to said dispersion, converting said dispersion into a thin continuous base web, preparing an overlayer dispersion from a similar film forming material which becomes substantially water insoluble when dry, adding a small quantity of a humectant to said overlayer dispersion, applying a thin coating of said overlayer dispersion upon the surface of said base web in permanently adhering relationship therewith to produce a composite web structure having a wet adhesive surface, heavily loading said wet surface with tobacco dust particles, drying said tobacco loaded web, removing loose tobacco from said tobacco dust loaded web, and forming said resulting tobacco web material into sheets of desired lengths and widths.

27. The method of making tobacco sheet material comprising forming a thin continuous adhesive web having a wet adhesive surface, applying tobacco dust substantially uniformly upon said surface of said web while adhesive to form a composite heavily loaded tobacco coated web drying said heavily loaded web, brushing loose tobacco from said composite tobacco dust coated web, ap-

Φ0003310 80

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

plying an adhesive to the tobacco coated surface of said tobacco web, bringing lengths of said web having adhesive tobacco coated surfaces into contacting engagement, and pressing said lengths together to form tobacco sheet material.

28. The method of making tobacco sheet material comprising forming an aqueous dispersion of adhesive film forming material into a thin wet adhesive film having an adhesive surface when said film is wet, said film being substantially water insoluble when dry, applying a heavy coating of finely divided tobacco to said wet adhesive film to form a tobacco loaded web and to adhere to said film a quantity of tobacco in an amount in excess of five times the weight of said film on a dry basis per unit area, and drying said web to form substantially water insoluble tobacco sheet material.

29. The method of making tobacco sheet material comprising forming an aqueous dispersion of adhesive film forming material into a thin wet adhesive film having an adhesive surface when said film is wet, said film being substantially water insoluble when dry, applying a heavy coating of finely divided tobacco to said wet adhesive film to form a tobacco loaded web and to adhere to said film a quantity of tobacco in an amount in excess of two and less than twenty times the weight of said film on a dry basis per unit area, and drying said web to form substantially water insoluble tobacco sheet material.

30. The method of making tobacco sheet material comprising forming a viscous aqueous film forming dispersion containing an adhesive, film forming material, which becomes substantially water insoluble when dry, into a thin base web having an exposed wet adhesive surface, coating said wet adhesive surface with finely divided tobacco to form a composite tobacco sheet material and drying said sheet material to render it substantially water insoluble.

31. The method of forming tobacco sheet material which comprises applying to the surface of a non fibrous layer of wet film forming material a layer of finely divided tobacco to form a composite lamellar sheet and drying said sheet to adhere a weight of said tobacco in excess of five times the weight of said film forming material on a dry basis per unit area.

32. The method of forming tobacco sheet material which comprises applying to the surface of a non fibrous layer of wet film forming material a layer of finely divided tobacco to form a composite lamellar sheet and drying said sheet to adhere a weight of said tobacco in excess of two and less than twenty times the weight of said film forming material on a dry basis per unit area.

33. The method of making tobacco sheet material comprising forming from an adhesive tobacco free film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, a thin continuous composite web having an adhesive surface, applying tobacco dust substantially uniformly upon said adhesive surface of said web and in excess of the amount of tobacco dust required to cover and to load said surface of said web, drying said tobacco coated composite web, and forming said resulting tobacco material into sheets.

34. The method of making tobacco sheet material comprising forming from a compound selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, a thin continuous tobacco free base web, applying an overlayer of film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, to said base web to form a composite web having an exposed wet surface, coating said exposed wet surface with tobacco particles to form a composite film, drying said tobacco coated composite film, moistening the uncoated faces of two sections of said tobacco coated film with an aqueous medium containing a film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, and assembling said sections with said moistened faces in contacting engagement to form laminated tobacco sheet material.

35. The method of producing tobacco sheet material comprising forming a thin, continuous tobacco free base web on a film forming surface from a film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, drying said web, applying an overlayer of a film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, over the surface of said base web, said overlayer adhering to and forming with said base web a thin composite web structure, heavily coating only one surface of said overlayer while wet with tobacco particles, drying said tobacco coated web, and laminating lengths of said composite tobacco web with the surfaces not coated with tobacco in face to face relation to form tobacco sheet material.

36. The method of producing tobacco sheet material comprising forming from an adhesive film forming material selected from the group consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, a thin, continuous tobacco free film on a film forming surface, applying to said film on said film forming surface while said film forming material is wet and adhesive, a loading in excess of five times the weight of said film in dry condition of finely divided tobacco, drying said tobacco coated film whereby said film forming material becomes substantially water insoluble and said tobacco coating becomes adhered to said film forming material, increasing the moisture content of said tobacco loaded film and removing said tobacco loaded film from said surface to form tobacco sheet material.

37. The method of producing tobacco sheet material comprising forming from an adhesive film forming material selected from the group consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, a thin, continuous tobacco free film on a film forming surface, applying to said film on said film forming surface while said film forming material is wet and adhesive, a loading in excess of two and less than twenty times the weight of said film in dry condition of finely divided tobacco, drying said tobacco coated film whereby said film forming material becomes substantially water insoluble and said tobacco coating becomes adhered to said film forming material, increasing the moisture content of said tobacco loaded film and removing said tobacco loaded film from said surface to form tobacco sheet material.

38. The method of producing tobacco sheet material comprising preparing a viscous adhesive film forming material selected from the class consisting of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose, water soluble salts of cellulose glycolic acid and water soluble salts of carboxymethyl hydroxyethyl cellulose, converting said film forming material into a thin, continuous base web, preparing an overlay from a similar less viscous adhesive film forming material, applying a thin coating of said overlay over a surface of said base web to produce a composite web structure having an adhesve surface,

0003310810

Source: https://www.industrydocuments.ucsf.edu/docs/xjnx0000

traveling surface and removing said loaded web from said surface.

48. The method of making tobacco sheet material comprising forming an aqueous stable dispersion of carboxymethyl hydroxyethyl cellulose, converting said dispersion into a thin continuous web, applying tobacco dust substantially uniformly over the surface of said web, drying said dust coated web and removing substantially all loose tobacco dust from said tobacco coated web.

49. The method of making tobacco sheet material comprising forming a tobacco free solution from a soluble salt of carboxymethyl cellulose, converting said solution into a thin continuous base web, preparing an overlayer from a similar film forming material, applying a thin coating of said overlayer over a surface of said base web to form a composite web structure having a wet adhesive surface, coating said web surface substantially uniformly with tobacco dust particles, drying said tobacco coated web and removing loose tobacco from said tobacco dust coated web to form said tobacco sheet material.

References Cited in the file of this patent

UNITED STATES PATENTS

21,558	Durell	Sept. 21, 1858
46,233	Hale	Feb. 7, 1865
50,038	Roffee	Sept. 19, 1865
88,519	Russell	Mar. 30, 1869
90,301	Posada	May 18, 1869
158,015	Barton	Dec. 22, 1874
203,766	Pickett	May 14, 1878
217,767	Bolles	July 22, 1879
239,661	Kimball	Apr. 5, 1881
267,764	Wood	Nov. 21, 1882
328,300	De Susini	Oct. 13, 1885
347,906	White	Aug. 24, 1886
865,012	Butler	Sept. 3, 1907
1,016,844	Moonelis	Feb. 6, 1912
1,164,114	Patterson	Dec. 14, 1915
1,591,170	Lutyens	July 6, 1926
1,716,250	Thiele	June 4, 1929
1,983,530	Brandenberger	Dec. 11, 1934
2,109,592	Macht et al.	Mar. 1, 1938
2,188,901	Hyatt	Feb. 6, 1940
2,232,012	Rooney et al.	Feb. 18, 1941
2,288,200	Meyer	June 30, 1942
2,331,830	Garber	Oct. 12, 1943
2,430,534	Rodli	Nov. 11, 1947
2,433,877	Wells et al.	Jan. 6, 1948
2,534,113	Egger	Dec. 12, 1950
2,544,247	Asaff et al.	Mar. 6, 1951
2,592,553	Frankenburg et al.	Apr. 15, 1952
2,592,554	Frankenburg	Apr. 15, 1952
2,598,680	Frankenburg	June 3, 1952
2,706,695	Frankenburg	Apr. 19, 1955

FOREIGN PATENTS

615	Great Britain	Mar. 4, 1865
8,366	Germany	Dec. 17, 1879
8,570	Great Britain	1886
UM 26,260 of 1926	Japan	June 3, 1926
186,719	Germany	June 6, 1907
231,078	Switzerland	June 1, 1944
376,763	Germany	June 4, 1923
617,694	Great Britain	Feb. 10, 1949
658,632	Germany	Apr. 6, 1938
661,168	Germany	June 13, 1938
853,719	Germany	Oct. 27, 1952

OTHER REFERENCES

Handbook of Plastics, by H. R. Simonds and C. Ellis, published 1943 by D. Van Nostrand Co., New York, N. Y. Pages 176, 309 and 692.

The Condensed Chemical Dictionary, published 1950 by Reinhold Publishing Corporation, New York, N. Y. Page 269. (Copy of this reference in Patent Office Library.)

UNITED STATES PATENT OFFICE 10003310824

CERTIFICATE OF CORRECTION

Patent No. 2,734,510 February 14, 1956

Gordon P. Hungerford et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, line 48, for "or",first occurrence, read --of--; column 18, line 21, list of references cited, under the heading "FOREIGN PATENTS" for "8,570" read --8,540--.

Signed and sealed this 9th day of October 1956.

10003310824

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

and coating said adhesive surface of said overlay while wet with finely ground tobacco particles to form tobacco sheet material.

39. The method of forming tobacco sheet material, comprising forming a thin, continuous tobacco free web from a film forming material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose and water soluble salts of carboxymethyl hydroxyethyl cellulose, then applying a coating of finely divided tobacco to one of the surfaces of said web while it is wet to form a tobacco coated web, drying said coated web, applying to the uncoated surface of said web an adhesive material selected from the class consisting of cellulose glycolic acid, water soluble salts of cellulose glycolic acid, carboxymethyl hydroxyethyl cellulose and water soluble salts of carboxymethyl hydroxyethyl cellulose to render said uncoated surface adhesive, applying a coating of finely divided tobacco to the adhesive uncoated surface of said web and drying said resulting tobacco sheet material.

40. The method of forming tobacco sheet material which comprises applying to the surface of a wet adhesive layer of cellulose glycolic acid, a layer of finely divided tobacco to form a composite lamellar sheet and drying said sheet to form tobacco sheet material.

41. The method of making tobacco sheet material comprising forming an aqueous dispersion of cellulose glycolic acid, casting said dispersion into an endless film on an endless traveling surface, coating said film on said surface with a dispersion of cellulose glycolic acid to provide said film with a wet adhesive overlayer, applying tobacco dust substantially uniformly over said wet overlayer in an amount sufficient to heavily load said film, drying said dust loaded film, removing substantially all loose tobacco dust from said tobacco loaded film and removing said film from said traveling film forming surface.

42. The method of producing tobacco sheet material comprising preparing an aqueous film forming dispersion of cellulose glycolic acid film forming material, adding a relatively small quantity of a filler material to a first portion of said dispersion to increase the tensile strength of the film produced therefrom, continuously forming said first portion of said dispersion on a substantially impermeable film forming surface into a thin, endless, water insoluble web, continuously applying the remainder of said dispersion as an overlayer of an aqueous insoluble film forming dispersion over the entire surface of said first portion of dispersion in permanently adhering relationship therewith to form a composite continuous web having an exposed wet surface, coating said exposed wet surface with finely divided tobacco particles in excess of five times the weight of said web on a dry basis per unit area, drying said heavily tobacco loaded composite continuous web whereby said web becomes water insoluble, brushing loose tobacco particles from said tobacco coated surface of said tobacco coated web, moistening said brushed tobacco coated composite web and removing it from said film forming surface, and then drying said web to form tobacco sheet material.

43. The method of producing tobacco sheet material comprising preparing an aqueous film forming dispersion of cellulose glycolic acid film forming material, adding a relatively small quantity of a filler material to a first portion of said dispersion to increase the tensile strength of the film produced therefrom, continuously forming said first portion of said dispersion on a substantially impermeable film forming surface into a thin, endless, water insoluble web, continuously applying the remainder of said dispersion as an overlayer of an aqueous insoluble film forming dispersion over the entire surface of said first portion of dispersion in permanently adhering relationship therewith to form a composite continuous web having an exposed wet surface, coating said exposed wet surface with finely divided tobacco particles in excess of two and less than twenty times the weight of said web on a dry basis per unit area, drying said heavily tobacco loaded composite continuous web whereby said web becomes water insoluble, brushing loose tobacco particles from said tobacco coated surface of said tobacco coated web, moistening said brushed tobacco coated composite web and removing it from said film forming surface, and then drying said web to form tobacco sheet material.

44. The method of forming tobacco sheet material comprising forming a tobacco free film forming composition of a soluble salt of cellulose glycolic acid, casting said composition on an endless traveling surface into a continuous wet web, applying tobacco dust substantially uniformly upon the wet web on said surface, said dust being applied in excess of the amount required to cover said surface of said web substantially uniformly, drying said dust loaded web, removing loose tobacco from said tobacco loaded web, moistening said web and removing said web from said traveling surface, drying said web, and forming said resulting tobacco material into sheets.

45. The method of making tobacco sheet material comprising forming an aqueous dispersion of cellulose glycolic acid, casting said dispersion into a continuous web on an endless traveling surface, coating said web on said surface with a dispersion of cellulose glycolic acid to provide said web with a wet adhesive overlayer to form a composite cellulose glycolic acid film having a wet adhesive surface, said film when dry being substantially water insoluble, applying tobacco dust to said wet overlayer in an amount sufficient to cover substantially uniformly the overlayer surface of said web, drying said dust loaded web, removing substantially all loose tobacco dust from said loaded tobacco web, removing said web from said traveling film forming surface, the tobacco dust adhering to and intimately associated with said web being greatly in excess by weight of the weight of said web of cellulose glycolic acid per unit area, subjecting said tobacco sheet material thus produced to heat and pressure to position projecting tobacco particles in substantially contiguous relationship relative to the plane of said composite web, moistening with an adhesive material the tobacco free faces of lengths of said tobacco coated composite web, arranging said lengths with said moistened faces in contacting engagement, pressing said lengths together to form laminated tobacco sheet material, and then brushing said faces of said laminated tobacco sheet material to remove loose tobacco therefrom.

46. The method of forming tobacco sheet material comprising forming a tobacco free film forming composition of a soluble salt of cellulose glycolic acid, casting said composition on an endless traveling surface into a wet continuous web, applying tobacco dust substantially uniformly upon the wet web on said surface, said dust being applied in excess of the amount required to load said web substantially uniformly with a predetermined quantity of tobacco per unit area of said web, drying said dust loaded web, removing loose tobacco from said tobacco loaded web, moistening said web and removing said web from said traveling surface, drying said web, treating the uncoated surface of said tobacco material web to render it tacky, arranging lengths of said treated web with said tacky surfaces in contacting engagement, and pressing said lengths together to form a laminated tobacco material web structure.

47. The method of making tobacco sheet material comprising forming a tobacco free film forming composition of a soluble salt of carboxymethyl hydroxyethyl cellulose, casting said composition on an endless traveling surface into a continuous web having a wet surface, applying tobacco dust upon the wet surface of said web, said dust being applied in excess of the amount required to cover substantially uniformly said surface of said web, drying said dust loaded web, removing loose tobacco from said tobacco loaded web, moistening said tobacco loaded web to facilitate its removal from said endless

Φ00033108Z

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

traveling surface and removing said loaded web from said surface.

48. The method of making tobacco sheet material comprising forming an aqueous stable dispersion of carboxymethyl hydroxyethyl cellulose, converting said dispersion into a thin continuous web, applying tobacco dust substantially uniformly over the surface of said web, drying said dust coated web and removing substantially all loose tobacco dust from said tobacco coated web.

49. The method of making tobacco sheet material comprising forming a tobacco free solution from a soluble salt of carboxymethyl cellulose, converting said solution into a thin continuous base web, preparing an overlayer from a similar film forming material, applying a thin coating of said overlayer over a surface of said base web to form a composite web structure having a wet adhesive surface, coating said web surface substantially uniformly with tobacco dust particles, drying said tobacco coated web and removing loose tobacco from said tobacco dust coated web to form said tobacco sheet material.

References Cited in the file of this patent

UNITED STATES PATENTS

21,558	Durell	Sept. 21, 1858
46,233	Hale	Feb. 7, 1865
50,038	Roffee	Sept. 19, 1865
88,519	Russell	Mar. 30, 1869
90,301	Posada	May 18, 1869
158,015	Barton	Dec. 22, 1874
203,766	Pickett	May 14, 1878
217,767	Bolles	July 22, 1879
239,661	Kimball	Apr. 5, 1881
267,764	Wood	Nov. 21, 1882
328,300	De Susini	Oct. 13, 1885
347,906	White	Aug. 24, 1886
865,012	Butler	Sept. 3, 1907
1,016,844	Moonelis	Feb. 6, 1912
1,164,114	Patterson	Dec. 14, 1915
1,591,170	Lutyens	July 6, 1926
1,716,250	Thiele	June 4, 1929
1,983,530	Brandenberger	Dec. 11, 1934
2,109,592	Macht et al.	Mar. 1, 1938
2,188,901	Hyatt	Feb. 6, 1940
2,232,012	Rooney et al.	Feb. 18, 1941
2,288,200	Meyer	June 30, 1942
2,331,830	Garber	Oct. 12, 1943
2,430,534	Rodli	Nov. 11, 1947
2,433,877	Wells et al.	Jan. 6, 1948
2,534,113	Egger	Dec. 12, 1950
2,544,247	Asaff et al.	Mar. 6, 1951
2,592,553	Frankenburg et al.	Apr. 15, 1952
2,592,554	Frankenburg	Apr. 15, 1952
2,598,680	Frankenburg	June 3, 1952
2,706,695	Frankenburg	Apr. 19, 1955

FOREIGN PATENTS

615	Great Britain	Mar. 4, 1865
8,366	Germany	Dec. 17, 1879
8,570	Great Britain	1886
UM 26,260 of 1926	Japan	June 3, 1926
186,719	Germany	June 6, 1907
231,078	Switzerland	June 1, 1944
376,763	Germany	June 4, 1923
617,694	Great Britain	Feb. 10, 1949
658,632	Germany	Apr. 6, 1938
661,168	Germany	June 13, 1938
853,719	Germany	Oct. 27, 1952

OTHER REFERENCES

Handbook of Plastics, by H. R. Simonds and C. Ellis, published 1943 by D. Van Nostrand Co., New York, N. Y. Pages 176, 309 and 692.

The Condensed Chemical Dictionary, published 1950 by Reinhold Publishing Corporation, New York, N. Y. Page 269. (Copy of this reference in Patent Office Library.)

UNITED STATES PATENT OFFICE 10003310824

CERTIFICATE OF CORRECTION

Patent No. 2,734,510 February 14, 1956

Gordon P. Hungerford et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, line 48, for "or",first occurrence, read --of--; column 18, line 21, list of references cited, under the heading "FOREIGN PATENTS" for "8,570" read --8,540--.

Signed and sealed this 9th day of October 1956.

10003310824

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

April 15, 1952 W. G. FRANKENBURG 2,592,554

RESILIENT TOBACCO PRODUCT AND METHOD OF MAKING THE SAME

Filed Aug. 24, 1946

Fig. 1

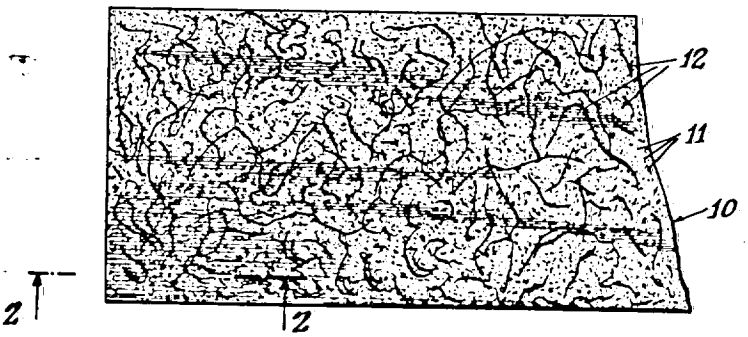


Fig. 2

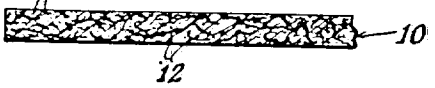


Fig. 3

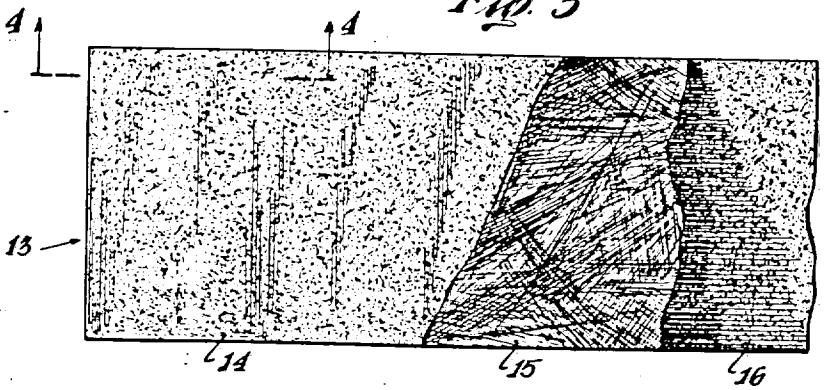
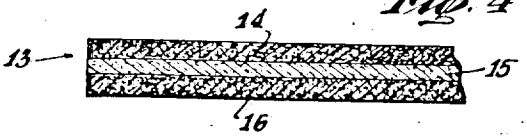


Fig. 4



INVENTOR.
Walter G. Frankenburg
BY
Paul W. Garbo
ATTORNEY

Φ000331084

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Patented Apr. 15, 1952 2,592,554

UNITED STATES PATENT OFFICE

2,592,554

RESILIENT TOBACCO PRODUCT AND METHOD OF MAKING THE SAME

Walter G. Frankenburg, Millersville, Pa., assignor to General Cigar Co., Inc., New York, N. Y., a corporation of New York

Application August 24, 1946, Serial No. 692,775

29 Claims. (Cl. 131—15)

1

This invention relates to tobacco products adapted for smoking and more particularly to products comprising tobacco in comminuted form.

This application is a continuation-in-part of my application Ser. No. 677,107, filed June 15, 1946, now abandoned.

Heretofore many proposals have been advanced with the object of converting finely divided tobacco into sheets or other coherent masses suitable for utilization in the manufacture of cigars and other smoking products. However, none of these suggestions has attained commercial recognition because in every instance the tobacco product failed to equal the original tobacco leaf form as to both smoking qualities and physical properties. With all of the proposals with which I am acquainted, the conversion of comminuted tobacco to a coherent or self-supporting body entailed such drastic processing of the comminuted tobacco that the smoking qualities, e. g., easy burning of the tobacco and pleasant aroma of the smoke, were substantially impaired if not entirely destroyed. Furthermore, these products were characterized by a considerably lower tensile strength and flexibility than the tobacco leaves from which they were prepared.

In my application Ser. No. 677,107, filed June 15, 1946, now abandoned, I have made a detailed disclosure of improved tobacco products comprising comminuted tobacco and a relatively small proportion of a water-soluble acid polysaccharide compound functioning as a binding agent or adhesive to hold the tobacco particles together in coherent masses. Judged in the light of the relatively small quantity of binding agent which I employ and the mild conditions under which adhesion is brought about between the tobacco particles so as not to detract from the smoking qualities of the tobacco so processed, the products of the invention of my copending application are remarkably coherent and self-supporting and, accordingly, represent a distinct advance over the prior art.

In the interests of better understanding and greater clarity, illustrative embodiments of my invention are presented hereinbelow in detail. In these examples, which are not to be construed in any restrictive sense, the proportions mentioned are all based on a common weight unit.

Example 1

Fifteen types and grades of leaf tobacco were weighed up in proportions dictated by the formula followed in the manufacture of a nationally known cigar. This weighed tobacco was passed

2

through a Raymond pulverizer operating with a screen of medium-size apertures. Substantially all of the comminuted tobacco could be screened through a 20-mesh sieve and approximately 50% of the material passed through a 40-mesh sieve. The powdered tobacco was thoroughly mixed to ensure good blending of the various types and grades. Obviously, at this point the tobacco had been blended with a degree of homogeneity impossible of attainment in conventional practice involving unpulverized tobacco. A highly viscous solution (like a heavy syrup) was prepared with 400 parts of water, 6 parts of refined sodium alginate and 10 parts of glycerine. One part of bentonite was added to 20 parts of water; when the bentonite suspension became homogeneous it was added to the foregoing aqueous alginate solution. The resulting composite liquid was added with stirring and kneading to 100 parts of the pulverized tobacco blend previously prepared. The pasty mass obtained by combining the liquid and the tobacco powder had a consistency like that of freshly prepared neat cement mortar and showed no tendency to exude liquid on standing. The pasty mass was placed on plate glass and covered with a sheet of wax paper. With the aid of a roller, the mass was pressed out between the wax paper and plate glass into a layer about 1/60 inch thick. The wax paper was removed and the plastic layer on the plate glass was transferred to a drying chamber in which air at a temperature of 50° C. was circulated. When the moisture content of the tobacco mass had been brought down to about 16%, the product was withdrawn from the drying chamber. The sheet of comminuted tobacco thus produced was self-supporting and fairly pliable. Conditioning of this sheet at 10° C. and at a relative humidity of 90%, increased its plasticity and flexibility considerably. The sheet was put up in the form of small rolls and, in other tests, in the form of irregularly shaped bunches which were then encased with a fine wrapper of Sumatra tobacco. In the cigars thus produced, it is clear that the roll or bunch of sheeted tobacco made in accordance with this invention replaced the filler leaf tobacco and binder leaves conventionally used in cigar manufacture. In blindfold smoking tests, the cigars of this example compared favorably, in the opinion of the average smoker, with ordinary cigars containing the same tobaccos. Experts considered the new cigars superior in that the smoke was of uniform quality and was freer of undesirable and irritating products of dry distillation and combustion; the latter feature appears to be

Φ00033108S

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

attributable to the presence of the bentonite in the cigar filler.

Example 2

One hundred parts of finely powdered tobacco (all particles passing through a 40-mesh screen) consisting of ground leaves of 8 types of flue-cured, air-cured and properly aged cigarette tobaccos were mixed with an aqueous solution of 500 parts of water, 1 part of sodium alginate, 2 parts of potassium pectate, 1 part of gum tragacanth, 8 parts of glycerine and 10 parts of diatomaceous earth. The thoroughly mixed paste was then extruded through a slit 2 inches long and 1/40 inch wide. The extruded ribbon of tobacco paste was deposited on a moving band of wire cloth and dried while on this band by means of a dry air stream at 50° C. After the ribbon of compacted tobacco powder was dried to a moisture content of 19%, it is cut into shreds of the ordinary size used in cigarette manufacture. These shreds were fed into a cigarette machine. The cigarettes made with this material were remarkable for the mildness and aroma of their smoke.

Example 3

One hundred parts of finely ground tobacco consisting of a blend of 12 different types and crops of American and Turkish, properly cured and aged tobaccos were thoroughly mixed with 250 parts of an aqueous solution of 5 parts of potassium alginate, 3 parts of sodium pectate, 10 parts of glycerine, 5 parts of sorbitol, 1 part of bentonite, ⅛ part of iron citrate and 5 parts of a flavoring solution which was a blend of several natural and synthetic aroma substances. The sorbitol supplemented the glycerine as plasticizer. The paste thus formed was extruded with the equipment used in Example 2 and dried in an air stream of 40° C. After reaching a moisture content of 25%, the tobacco ribbon was cut into pieces of the size ordinarily used for pipe tobacco. This blended pipe tobacco had a much more even burn, a better fire-holding capacity and a better retention of flavor than a control sample of a conventional rough mixture of pieces of the same tobaccos. Furthermore, its smoking quality was characterized by a high degree of mildness and a pleasant and uniform aroma.

The present invention is not to be confused with the many suggestions made in prior patents of which a large number issued during the period of 1860 to 1900. These prior proposals generally treated waste tobacco in substantially the same way in which wood, rag, straw, bagasse, etc., are pulped in the manufacture of paper. Some of the later patents acknowledge that the tobacco so converted to paper had lost practically all of the constituents which make tobacco suitable for smoking, and attempted to correct this deficiency by impregnating the tobacco paper with a concentrated decoction obtained by boiling a suspension of tobacco in water. However, all of these earlier schemes failed because it was not appreciated that tobacco and tobacco extracts are inherently delicate and unstable and that even moderate variations in such factors as temperature and hydrogen-ion concentration may adversely affect the tobacco or tobacco extracts by causing decomposition, oxidation, polymerization or other chemical reactions of the compounds in tobacco. In contrast to these prior unsuccessful efforts, the present invention involves the mildest conditions of treatment and avoids the pulping of the tobacco in water or other processing liquid which would extract many soluble tobacco compounds and thus leave an impoverished and deteriorated tobacco product.

Two or more acid polysaccharide compounds are sometimes used in compounding a tobacco product of this invention since certain advantages, e. g., increased thickening of the aqueous solution, may be obtained with mixed polysaccharides.

In spite of the improvements achieved, these products are not wholly satisfactory from the point of view of physical properties particularly when they are utilized in automatic machines for the production of cigars and the like.

It is an object of this invention to improve the physical properties of products made from comminuted tobacco without detrimentally influencing the smoking characteristics of the original tobacco.

Another object is to facilitate materially the manufacture of cigars from sheets or other coherent bodies of comminuted tobacco.

These and further objects of my invention will become apparent from the description which follows.

In accordance with this invention, tobacco products in the form of coherent masses of comminuted tobacco are improved in physical properties by combining a minor proportion of glass fibers with the tobacco mass. I have found that fine fibers of glass of the order of 0.0002" in diameter resembling silk threads not only in appearance but also in softness and flexibility contribute appreciable tensile strength, flexibility and resiliency to coherent masses of comminuted tobacco in which they have been incorporated. While the proportion of glass fibers may vary over a broad range, it is generally satisfactory to use from about 1 to 15% of glass fibers based on the weight of the tobacco. Preferably, from about 2 to 5% by weight of glass fibers are combined with the finely divided tobacco. The fibers may be arranged in the coherent mass of comminuted tobacco either as more or less individual fibers uniformly distributed throughout the tobacco mass or as a lamina of felted fibers carrying an adhering layer of ground tobacco on one or both of its faces.

When loose fibers are mixed with comminuted tobacco and converted into coherent, self-supporting bodies by means of a suitable binding agent or adhesive, the glass fibers usually will have a length ranging from about ½ to 2½" with a major portion of the fibers measuring from about 1 to 1½" in length. Where the glass fibers are used in the form of a felted mat, they may be considerably longer. Glass fiber mats have reached a high state of technical development and are commercially available. Such mats are generally supplied with the fibers bonded together by a minor proportion of adhesive, e. g., resin or starch, and, for most purposes of this invention, it is advisable to select mats of not more than about 0.010" thickness, preferably of about 0.003 to 0.006" thickness.

For more detailed description and further clarification of my invention, reference is made to the accompanying drawing of which:

Figure 1 is a plan view of one type of tobacco sheet prepared in accordance with the invention;

Figure 2 is a magnified sectional view taken along the line 2—2 of Figure 1;

Figure 3 is a plan view of another form of product of this invention; and

Φ00033108

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Figure 4 is a magnified sectional view taken along the line 4—4 of Figure 3.

In Figure 1, the numeral 10 designates a coherent, self-supporting sheet comprising tobacco particles 11 and glass fibers 12 in intimate and uniform admixture. The tobacco particles 11 and glass fibers 12 are held together by a small proportion of a binding substance. The glass fibers 12 act to improve the physical properties of the sheet 10, the tensile strength, flexibility and resiliency being notably good. In effect, the glass fibers function in a coherent mass of comminuted tobacco in much the same manner as do reinforcing steel rods in concrete masses.

Figure 2 presents an enlarged cross-section of sheet 10 to show the random orientation and uniform distribution of glass fibers 12 throughout the thickness of sheet 10. It is, therefore, clear from both Figure 1 and Figure 2 that the glass fibers form a three-dimensional reinforcing network for the adhering tobacco particles 11.

In Figure 3, the numeral 13 refers to a laminated sheet consisting of a top layer 14 of finely divided tobacco held together and to the underlying layer by an adhesive, an intermediate layer 15 of matted glass fibers, and a bottom layer 16 of tobacco similar to top layer 14.

The enlarged sectional view of laminated sheet 13 represented by Figure 4 shows schematically that the superficial tobacco layers 14 and 16 are bonded not only to the faces of the glass fiber mat 15 but also to each other through the interstices of the thin, porous mat 15. Because the tobacco layers 14 and 16 are anchored to and through the intermediate layer 15 of glass fibers, the three laminae function as a unitary sheet. As in the product depicted in Figures 1 and 2, the glass fiber mat 15 is the reinforcing element of sheet 13.

More specifically, a product of the type shown in Figures 1 and 2 is prepared as follows. Several types and grades of leaf tobacco are weighed up in proportions dictated by the formula followed in the manufacture of a nationally known cigar. This weighed tobacco is passed through a Raymond pulverizer operating with a screen of medium-size apertures. Substantially all of the comminuted tobacco can be screened through a 20-mesh sieve and approximately 50% of the material passes through a 40-mesh sieve. With 100 parts by weight of the thus pulverized and blended tobacco there are uniformly mixed 2½ parts of glass fibers having an average diameter of 0.00022" and an average length of about 1½". A highly viscous solution (like a heavy syrup) is prepared with 400 parts of water, 6 parts of refined sodium alginate and 5 parts of glycerine. The viscous solution is added with stirring and kneading to the dry mixture of pulverized tobacco and glass fibers previously prepared. A pasty mass is obtained having a consistency similar to that of the freshly prepared neat cement mortar and there is no evidence of liquid exuding from the paste. The pasty mass is placed on plate glass and covered with a sheet of wax paper. With the air of a roller, the mass is pressed out between the wax paper and plate glass into a layer about 1/40" thick. The wax paper is removed and the plastic layer on the plate glass is transferred to a drying oven in which air at a temperature of 50° C. is circulated. When the moisture content of the tobacco mass has been brought down to about 15%, the product is withdrawn from the drying chamber and is lifted from the plate glass. The sheet of comminuted tobacco thus produced is self-supporting and remarkably pliable.

As an example of a product of my invention of the type shown in Figures 3 and 4, 100 parts by weight of finely powdered tobacco (all particles passing through a 40-mesh screen) consisting of ground leaves of 8 types of air-cured, sweated and properly aged tobaccos are mixed with an aqueous solution of 500 parts of water, 1 part of sodium alginate, 2 parts of potassium pectate, 1 part of gum tragacanth, 6 parts of glycerine and 5 parts of diatomaceous earth. The thoroughly mixed paste is then applied to both faces of a glass fiber mat approximately 0.005" thick and weighing about 1.5 grams per square foot. The quantity of tobacco paste spread on the glass fiber mat is controlled so that, on the dry basis, the glass fibers of the composite sheet represent about 5% of the weight of the tobacco. The wet tobacco sheet is brought to a moisture content of about 17% by exposure to a circulating stream of dry air at a temperature of about 50° C. After the drying operation, the sheet can be handled with ease and shows considerable flexibility and resiliency.

In still another example, 100 parts by weight of a finely ground mixture of American and Cuban tobaccos and 3 parts of silky glass fibers ranging in length from about ½ to 2" are thoroughly mixed with a viscous slurry consisting of 300 parts of water, 4 parts of potassium alginate, 3 parts of sodium pectate, 4 parts of glycerine, 2 parts of sorbitol and 1 part of bentonite. The paste thus formed is extruded through a slit 2" long and 1/40" wide. The extruded ribbon of tobacco paste is deposited on a moving band of wire cloth and dried while on this band by means of a circulating dry air stream at a temperature of 45° C. After the ribbon has been conditioned to a moisture content of approximately 14% it can be subjected to mechanical operations, such as winding in rolls, inasmuch as it has a fairly high tensile strength and flexibility.

A further example illustrates the production of a tobacco sheet which is a desirable replacement for the "binder leaf" conventionally used in cigar manufacture to wrap up and hold together the loose pieces of filler tobacco in roll form. It is obvious that a sheet utilized as binder leaf must have good tensile strength, pliability and resistance to crumbling. Such a sheet is prepared by kneading 100 parts by weight of a finely ground Connecticut binder tobacco with a mixture of 300 parts of water, 5½ parts of sodium alginate, 4 parts of glycerine and 8 parts of diatomaceous earth. A stiff paste is obtained which is then softened by addition with continued kneading of a warm solution (40° C.) consisting of 100 parts of water and 3 parts of agar-agar, the solution having been previously prepared by dissolving the agar-agar in water at a temperature of 90° C. The resulting smooth paste is spread on both sides of a glass fiber mat approximately 0.008" thick. The tobacco-coated mat is moved slowly through a drying tunnel at a temperature of 45° C. until the material has a residual moisture content of about 19% by weight. The finished sheet carries about 25 grams of tobacco per square foot of glass fiber mat which weighs about 2.2 grams per square foot. The tensile strength and resiliency of this sheet are at least equal, if not superior, to those of binder leaves. It can be readily cut into pieces of exactly the right shape required for binder leaves so that in contrast to conventional cigar production with "natural"

Φ00331087

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

leaves, only a negligible amount of trimmings are formed. Such trimmings do not necessarily represent waste material since by my invention they may be reworked into new sheets.

As illustrated in the immediately preceding example, I have found it advantageous to use a limited quantity of agar-agar, generally not more than about 5% by weight of the tobacco. It appears that the agar-agar dispersed throughout the mass of comminuted tobacco as a water solution forms a fibrous structure in the finished tobacco product when the water is expelled by evaporation. This belief is based on the observation that agar-agar improves the physical properties of tobacco sheets prepared from finely divided tobacco and a binding agent, e. g., sodium alginate, even in the absence of glass fibers. When used in a mixture which includes glass fibers, agar-agar supplements glass fibers in their function of improving the tensile strength, resiliency, flexibility, etc., of the coherent tobacco product.

When each of the products of the foregoing examples is compared with a product made with the same formula proportions under the same processing conditions, except that the glass fibers are omitted, it is evident that the glass fibers contribute materially to the tensile strength, resiliency and flexibility of the product. Thus, while a given coherent sheet of comminuted tobacco will generally crumble when rolled up between the fingers, the same product with a minor proportion of glass fibers, say 2 to 5% by weight of the tobacco, will withstand rolling up between the fingers substantially without evidence of cracking. This distinct improvement in the physical properties of sheets or other coherent forms of comminuted tobacco is of significant importance in permitting the utilization of these coherent tobacco bodies in mechanical operations, such as the bunching and rolling operations encountered in the current manufacture of cigars.

From experience I have found it advisable to employ a plasticizer for the coherent body of finely divided tobacco. This accounts for the presence of glycerine and sorbitol in the foregoing examples of my invention. Additions of glycerine of the order of 2% to 15% by weight, based on the weight of dry tobacco used, to mixtures of comminuted tobacco and aqueous solutions of acid polysaccharide compounds with or without bentonite exert an appreciable plasticizing effect.

Furthermore, I have found it advantageous to add a small proportion of bentonite or other water-swelling clay to the mixture prepared for forming a continuous, self-supporting body of comminuted tobacco. Generally, additions of the order of 1 to 2% by weight of bentonite, based on the weight of dry tobacco powder used, are recommended. It appears that bentonite on swelling in the wet plastic mass of tobacco tends to form a coherent inorganic skeleton or reinforcing network which supplements the fine glass fibers in improving the physical properties of the final product. Moreover, the bentonite tends to absorb or filter out undesirable tarry constituents and alkaloids of tobacco smoke as it is drawn through the unburned portion of the bentonite-containing tobacco product.

While any desired adhesive or binding substance in liquid form may be utilized in preparing the products of my invention, I favor the use of the water-soluble acid polysaccharide compounds disclosed in my application Ser. No. 677,107, filed June 15, 1946, now abandoned. As used in my copending application and in this specification and appended claims, the term, acid polysaccharide compound, embraces algins, pectins and plant gums which are characterized by a molecular structure involving uronic acids, as well as polysaccharic and polysaccharinic compounds. The acid polysaccharide compounds may be in the form of acids, salts and esters. The acid polysaccharide compounds of the type involving uronic acids, sometimes referred to as polyuronides (cr. J. A. C. S. 52, 2474 (1930)), are often associated with pentosans and are utilizable in such form in this invention. The selected acid polysaccharide compound must be such that a small quantity, i. e., not exceeding about 5% by weight, added to water will form a solution having a viscosity of at least 1500 centipoises at a temperature of 25° C. Preferably, the acid polysaccharide compound should be one that yields an aqueous solution of equal or greater viscosity when present in only about 2% concentration.

The quantity of viscous polysaccharide solution which is admixed with the powdered tobacco is limited to that which yields a plastic mass having a consistency approximating that of a good neat cement mortar. An excess of solution detectable by the tendency of the plastic mass to exude liquid should be avoided since any substantial loss of liquid reflects a loss of extractable constituents in the tobacco and consequent alteration of the original smoking qualities of the tobacco. Usually, one part by weight of comminuted tobacco and about two to six parts by weight of the aqueous polysaccharide solution will form a paste of the desired consistency; the finished tobacco product contains less than 20% by weight of the polysaccharide, and frequently less than 10%. My preferred tobacco compositions contain only about 6% by weight of admixed polysaccharide.

Of the several acid polysaccharide compounds meeting my requirements, the algin and pectin families are notably satisfactory. The water-soluble derivatives of these polysaccharides, such as alginic and pectic acids and their sodium and potassium salts, are particularly desirable. It is well to note that algin and pectin and their derivations resemble the family of gums which on hydrolysis give uronic acids, e. g., glucuronic and galacturonic acids.

Acid polysaccharide compounds being compounds made up entirely of carbon, hydrogen and oxygen atoms are well suited for incorporation in tobacco compositions intended for smoking. It has been found that the dry distillation and the incomplete combustion of these polysaccharides yield substantially no substance of disagreeable or irritating properties. The complete combustion of acid polysaccharide compounds yields carbon dioxide and water vapor which are the products of combustion of many natural constituents of tobacco. This smoking compatibility of acid polysaccharide compounds and tobacco should be safeguarded by the exercise of care in selecting polysaccharides in a state of refinement. The refined products should be free of any appreciable quantities of extraneous matter containing compounds of nitrogen, particularly proteins, and compounds of sulfur, phosphorus and the halogens; in short, compounds giving undesirable products of combustion or dry distillation should be avoided. Where the tobacco paste is prepared with a water solution of an acid poly-

0000331088

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

saccharide compound and this paste is applied to a mat of glass fibers, it is advantageous to have the glass fibers bonded together with the same acid polysaccharide compound used in the tobacco paste.

In the interests of producing coherent masses of comminuted tobacco having good porosity to facilitate smoking, it is advisable to include diatomaceous earth in the tobacco composition. Additions of diatomaceous earth of 10 to 25% of the weight of the powdered tobacco result in products of relatively high porosity and low density. With some tobaccos, this favors combustion and high aroma content in the smoke.

The tobacco products prepared in accordance with this invention may also include other valuable additives, such as minute quantities of combustion catalysts, e. g., finely dispersed oxides of iron and copper, organic substances to impart desired flavors to the smoke of the resulting tobacco product, and wetting agents which facilitate the attainment of intimate contact and cohesion between the tobacco particles, glass fibers, additives, and the binding agent.

The term, glass, is used in this specification and the appended claims in its broadest sense. Glass is commonly defined as an amorphous substance, usually transparent or translucent and ordinarily comprising chiefly a mixture of silicates, but in some cases, of borates, phosphates, etc. Glass is also identified as a super-cooled liquid. It is well to note at this point that the fine fibers of glass which I employ to reinforce coherent bodies of comminuted tobacco are, contrary to popular belief, completely harmless. The glass fibers are so soft and pliable that even when the end of a cigar containing them is chewed, their presence is not felt by the lips or tongue. When a tobacco product containing glass fibers is burned, the fine fibers are softened and disintegrated within the glowing zone so that the glass residue is not sensibly different from the rest of the tobacco ash. Obviously, during the combustion of the tobacco, the glass fibers do not give off any products which contaminate or adulterate the smoke.

Hereinabove it has been emphasized that glass fibers increase the resiliency of coherent bodies of comminuted tobacco. In the manufacture of cigars and the like, this effect is important not only because the finished product has the pleasing and natural resilient feel of cigars made of leaf tobacco (not comminuted) but also because resiliency prevents or minimizes packing of the tobacco within the cigar. Consolidation of the tobacco in cigars or other smoking products is undesirable since the voids are reduced and a low content of voids in such products interferes with the easy drawing of smoke therethrough. It is clear that the products of this invention may be utilized in place of filler, binder or wrapper tobacco leaves commonly used in the production of cigars.

Those skilled in the art will visualize many other modifications and variations of the invention set forth hereinabove without departing from its spirit and scope. Accordingly, the claims should not be interpreted in any restrictive sense other than that imposed by the limitations recited within the claims.

What I claim is:

1. In the manufacture of cigars, the improvement which comprises dry-grinding tobacco, forming a paste of said dry-ground tobacco with a quantity of viscous aqueous solution of an acid polysaccharide compound sufficient to form a cohesive paste but insufficient to permit exudation of said viscous solution from said paste, said viscous solution containing not more than about 5% by weight of said polysaccharide and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., coating a thin mat of fine glass fibers with said paste, drying said coated mat, and using said dried, coated mat as binder leaf in the manufacture of cigars.

2. The process of claim 1 wherein the acid polysaccharide compound is a member of the family of algin compounds.

3. A tobacco product in physically continuous and coherent form characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble acid polysaccharide compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 5% by weight of said acid polysaccharide is dissolved in water, and a minor proportion, lesser than said minor proportion of acid polysaccharide and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers, said acid polysaccharide and said glass fibers holding the particles of said tobacco together in said physically continuous and coherent form.

4. A tobacco product in physically continuous and coherent form characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble algin compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 5% by weight of said algin compound is dissolved in water, and a minor proportion, lesser than said minor proportion of algin compound and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers, said algin compound and said glass fibers holding the particles of said tobacco together in said physically continuous and coherent form.

5. A tobacco product in physically continuous and coherent form characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 10% by weight of said tobacco, of a water-soluble alkali metal alginate having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 2% by weight of said alginate is dissolved in water, and a minor proportion, lesser than said minor proportion of alginate and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers, said alginate and said glass fibers holding the particles of said tobacco together in said physically continuous and coherent form.

6. A thin tobacco sheet characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble algin compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 2% by weight of said algin compound is dissolved in water, and a minor proportion, lesser than said minor proportion of algin com-

Φ0003310 89

Source: https://www.industrydocuments.ucsf.edu/docs/xjnc0000

pound and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers, said algin compound and said glass fibers holding the particles of said tobacco together in the form of said thin tobacco sheet.

7. A thin tobacco sheet characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble algin compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 5% by weight of said algin compound is dissolved in water, and a minor proportion, lesser than said minor proportion of algin compound and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers in matted form, the particles of said tobacco being bonded by said algin compound to said matted glass fibers and thus forming said thin tobacco sheet.

8. A thin tobacco sheet characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble sodium alginate having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 2% by weight of said sodium alginate is dissolved in water, and a minor proportion, lesser than said minor proportion of sodium alginate and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers in matted form, the particles of said tobacco being bonded by said sodium alginate to said matted glass fibers and thus forming said thin tobacco sheet.

9. In the manufacture of smoking products, the improvement which comprises dry-grinding tobacco, forming a paste of said dry-ground tobacco with a quantity of viscous aqueous solution of an acid polysaccharide compound sufficient to form a cohesive paste but insufficient to permit exudation of said viscous solution from said paste, said viscous solution containing not more than about 5% by weight of said polysaccharide and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., combining said paste with a minor proportion of fine flexible glass fibers, said minor proportion not exceeding 5% by weight of said tobacco, pressing and drying said paste containing the glass fibers into a desired, coherent form, and utilizing said coherent form of tobacco in the manufacture of smoking products.

10. The process of claim 9 wherein the acid polysaccharide compound is a member of the family of algin compounds.

11. In the manufacture of smoking products, the improvement which comprises dry-grinding tobacco, forming a paste of said dry-ground tobacco with a quantity of viscous aqueous solution of an acid polysaccharide compound sufficient to form a cohesive paste but insufficient to permit exudation of said viscous solution from said paste, said viscous solution containing not more than about 2% by weight of said polysaccharide and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., combining said paste with a minor proportion of fine flexible glass fibers, said minor proportion not exceeding 5% by weight of said tobacco, pressing and drying said paste containing the glass fibers into a desired, coherent form, and utilizing said coherent form of tobacco in the manufacture of smoking products.

12. The process of claim 11 wherein the acid polysaccharide compound is an alkali metal alginate.

13. A tobacco product in physically continuous and coherent form characterized by flexibility and adaptability for smoking, which comprises a predominant proportion of dry-ground tobacco, a minor proportion, not exceeding 20% by weight of said tobacco, of a water-soluble binding agent innocuous to the smoking qualities of said tobacco and having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than 5% by weight of said binding agent is dissolved in water, and a minor proportion, lesser than said minor proportion of binding agent and not exceeding 5% by weight of said tobacco, of fine flexible glass fibers, said binding agent and said glass fibers holding the particles of said tobacco together in said physically continuous and coherent form.

14. The tobacco product of claim 13 wherein said glass fibers are in matted form.

15. A tobacco product suited for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not more than 20% by weight of said tobacco, of a water-soluble acid polysaccharide compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at 25° C. when not more than about 5% by weight of said polysaccharide is dissolved in water, said polysaccharide functioning to hold said dry-ground tobacco as a coherent mass.

16. A tobacco product suited for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not more than 10% by weight of said tobacco, of a water-soluble acid polysaccharide compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at 25° C. when not more than about 2% by weight of said polysaccharide is dissolved in water, said polysaccharide functioning to hold said dry-ground tobacco as a coherent mass.

17. In the manufacture of cigars, the improvement which comprises dry-grinding tobacco, mixing said dry-ground tobacco with a quantity of an aqueous solution of an acid polysaccharide compound sufficient to form a cohesive paste but insufficient to permit exudation of said solution from said paste, said solution containing not more than about 5% by weight of said polysaccharide and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., pressing and drying said paste into a desired, coherent form, and utilizing said coherent form of tobacco in the manufacture of cigars.

18. The process of adapting and blending a plurality of tobaccos for use in smoking products, which comprises dry-grinding said tobaccos, mixing said dry-ground tobaccos with a quantity of an aqueous solution of an acid polysaccharide compound sufficient to form a cohesive paste but insufficient to permit exudation of said solution from said paste, said solution containing not more than about 2% by weight of said polysaccharide and having a viscosity of not less than 1500 centipoises at a temperature of 25% C., and pressing and drying said paste into a coherent form adapted for use in smoking products.

19. The improved process of converting tobacco into a physically continuous and coherent form adapted for smoking, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of a binding

Φ0003310900

Source: https://www.industrydocuments.ucsf.edu/docs/kpnf0000

agent innocuous to the smoking qualities of said tobacco in proportions to form a cohesive paste substantially free of exudation of said viscous aqueous solution, said viscous aqueous solution containing not more than about 5% by weight of said binding agent and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., and shaping and drying said paste into a desired, physically continuous and coherent form adapted for smoking.

20. The improved process of claim 19 wherein the binding agent is an alkali metal alginate.

21. The improved process of converting tobacco into a thin sheet adapted for the manufacture of cigars, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of sodium alginate in proportions to form a cohesive paste substantially free of exudation of said viscous aqueous solution, said viscous aqueous solution containing not more than about 2% by weight of said alginate and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., and forming and drying said paste into a thin sheet adapted for the manufacture of cigars.

22. A tobacco product suited for smoking, which comprises a predominant proportion of dry-ground tobacco and minor additions of not more than about 10% by weight of an alkali metal alginate having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight of said alginate is dissolved in water, and about 2% to 15% by weight of glycerine, all said additions being based on the weight of said tobacco and being homogeneously mixed therewith to hold said dry-ground tobacco as a coherent, self-supporting mass.

23. A tobacco product suited for smoking, which comprises a predominant proportion of dry-ground tobacco and a minor proportion, not more than 20% by weight of said tobacco, of a water-soluble acid polysaccharide compound having the property of forming an aqueous solution with a viscosity of at least 1500 centipoises at a temperature of 25° C. when not more than about 2% by weight of said polysaccharide is dissolved in water, said polysaccharide functioning to hold said dry-ground tobacco as a coherent mass.

24. The tobacco product of claim 23 wherein the water-soluble acid polysaccharide compound is an alkali metal alginate.

25. The tobacco product of claim 24 wherein there has been incorporated about 2% to 15% by weight of glycerine, based on the weight of the tobacco.

26. The improved process of converting tobacco into a physically continuous and coherent form adapted for smoking, which comprises dry-grinding tobacco, mixing the dry-ground tobacco and a viscous aqueous solution of a binding agent innocuous to the smoking qualities of said tobacco in proportions to form a cohesive paste substantially free of exudation of said viscous aqueous solution, said viscous aqueous solution containing not more than 2% by weight of said binding agent and having a viscosity of not less than 1500 centipoises at a temperature of 25° C., and shaping and drying said paste into a desired, physically continuous and coherent form adapted for smoking.

27. The improved process of claim 26 wherein the binding agent is an alkali metal alginate.

28. The improved process of claim 26 wherein glycerine, in an amount corresponding to about 2% to 15% of the weight of the dry-ground tobacco, is admixed with said viscous aqueous solution.

29. The tobacco product of claim 15 wherein there has been incorporated about 2% to 15% by weight of glycerine, based on the weight of the dry-ground tobacco.

WALTER G. FRANKENBURG.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
21,558	Durell	Sept. 21, 1858
64,591	Stayman	May 7, 1867
217,767	Bolles	July 22, 1879
341,072	Sanford	May 4, 1886
637,419	Richmond	Nov. 21, 1899
872,987	Capehart	Dec. 3, 1907
1,016,844	Moonelis	Feb. 6, 1912
1,814,986	Walsh	July 14, 1931
1,954,109	Whitaker	Apr. 10, 1934
1,972,718	Sharlit	Sept. 4, 1934
2,160,107	Maxwell et al.	May 30, 1939
2,307,088	Whiteley	Jan. 5, 1943
2,433,877	Wells et al.	Jan. 6, 1948

FOREIGN PATENTS

Number	Country	Date
282,369	Great Britain	Nov. 30, 1927
879,939	France	Mar. 9, 1943

OTHER REFERENCES

The Manufacture of Pulp Paper, vol. IV, 1928, pages 50–51. (Copy in Div. 56.)

Journal of the Franklin Institute, June, 1946, pp. 457 and 458. (Copy in Div. 56.)

0000331091

Source: https://www.industrydocuments.ucsf.edu/docs/xjm40000

PATENT SPECIFICATION

698,948

Date of Application and filing Complete Specification: Oct. 27, 1950. No. 26240/50.

Application made in United States of America on Dec. 2, 1949.

Complete Specification Published: Oct. 28, 1953.

Index at acceptance:—Classes 2(ii), A4(b2:c2:x), C1.

COMPLETE SPECIFICATION

Aqueous dispersions of Cellulose Glycolic acid or Carboxymethyl Hydroxyethyl cellulose and Water-insoluble coatings Films and Adhesives made therefrom

We, AMERICAN MACHINE & FOUNDRY CO., a corporation organized and existing under the laws of the State of New Jersey, located at 511 Fifth Avenue, New York City, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing aqueous dispersions of cellulose glycolic acid, and of its derivative half ethers with ethylene glycol, known in the art as carboxymethyl hydroxyethyl cellulose, and to stable aqueous dispersions of such compounds, and also to insoluble coatings, sizings, adhesives, and to insoluble films, webs, sheets, and strips produced therefrom.

It is known in the art to employ the alkali metal salts or ammonium salt of cellulose glycolic acid for many purposes. These salts readily dissolve in water to form viscous solutions which have film forming properties and are also useful as thickeners, sizing agents, and stabilizers for a variety of dispersions. For example, sodium cellulose glycolate, which is also known in the trade as the sodium salt of carboxymethylcellulose, "CMC", cellulose gum, and "Carboxymethocel", has been employed in sizing and finishing of textile yarns and fabrics, in grease proofing of paper-board and related products, with detergents to eliminate dirt redeposition, in coating paper to improve physical properties, and in many other compositions, such as paints, pastes, pigments, creams and inks for viscosity adjustment and stabilization.

In spite of their many desirable properties and varied applications, the soluble salts of cellulose glycolic acid have serious limitations, particularly in the form of sheets and webs or when used in sizings, coating and adhesive compositions requiring water insensitivity or insolubility and resistance to deterioration by contact with moisture in the air. For example, sodium cellulose glycolate sheets readily dissolve in water, or become sticky when exposed to high relative humidity in the atmosphere due to moisture absorption. Similar difficulties are encountered with textile yarns, fabrics and the like containing a sizing or coating of sodium cellulose glycolate.

In some instances these difficulties can be overcome by forming a soluble cellulose glycolate into the desired shape, such as a film, thread, filament or coating, and treating the wet shape with a coagulating solution, such as an acid solution or a solution of a precipitating salt, such as aluminium or zirconium salt, thereby forming in situ insoluble cellulose glycolic acid, aluminum cellulose glycolate, or zirconium cellulose glycolate, respectively. Since secondary reaction products are formed through the release of the cation from the cellulose glycolate and the anion from the precipitating salt or acid, and are present in the insolubilized shape together with excess precipitating agent, it is sometimes preferred to remove these by rinsing or washing of the shape. In most cases, the wet shape of soluble cellulose glycolate orignially formed is dried before the insolubilizing agent is applied. Removal of the secondary reaction products and excess precipitating agent is more difficult when the shape is dried before treatment than when it is not dried, but the shape is much less difficult to handle mechanically when dried than when wet. Frequently, however, such treatments are undesirable, impractical or impossible for various reasons. The presence of acid, heavy metal ions, or alkali metal salts may be objectionable and in some cases it is mechanically impractical to remove these by rinsing or washing. Moreover, performing the mechanical operations involved is, in many cases, very complicated and expensive, and thus insolubilization by these techniques increases

Source: https://www.industrydocuments.ucsf.edu/docs/xjmn0000

the cost of the product.

Where insolubility of the glycolate used is required, however, insolubilization operations, as above described, have been unavoidable heretofore, since dry insoluble cellulose glycolic acid or its heavy metal or other insoluble salts, as presently known to the art, could not be dispersed in a suitable form and therefore could not be applied or used directly. For example, pure cellulose glycolic acid cannot be dispersed in water without reconversion to a soluble salt, such as by the addition of caustic alkali or ammonia.

The present invention constitutes a solution of this problem because it makes possible the formation of a water dispersion of cellulose glycolic acid or of carboxymethyl hydroxyethyl cellulose which has substantially all of the desirable characteristics and properties of a solution of a soluble salt of cellulose glycolic acid for various applications in addition to the desired water insolubility of the free cellulose glycolic acid. A water dispersion made in accordance with the invention, when used in treating paper, paperboard, textile yarns and textile products, and in the formation of films, webs and strips, results in final products in which the coatings and sizings are insoluble, as are the films, webs, sheets and strips made therefrom. This obviates the necessity of converting in situ the soluble salt of cellulose glycolic acid into insoluble cellulose glycolic acid in a separate operation after impregnation of the textile or formation of a film, and therefore simplifies, expedites and makes less expensive the production of the desired final products, and in some cases, makes it possible to produce products which it is not possible to make by the presently available techniques.

It is an object of this invention, therefore, to provide a novel method for forming aqueous dispersions of cellulose glycolic acid and carboxymethyl hydroxyethyl celluose.

It is a further object of the invention to develop a novel method of forming a dispersion of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose suitable for use as sizing, thickening, coating and adhesive compositions, and also as a film forming dispersion, by producing a water insoluble form of cellulose glycolic acid in the form of a stable colloidal dispersion which can then be used to produce insoluble, self-supporting continuous sheets and films and also to provide paper, paperboard, textile yarns, and textile fabrics with insoluble coatings, sizings and adhesives.

The invention consists in the novel method of forming a stable aqueous dispersion of cellulose glycolic acid by the acidification of an aqueous solution of a soluble salt of cellulose glycolic acid to precipitate insoluble cellulose glycolic acid and then converting the freshly precipitated, highly hydrated, insoluble cellulose glycolic acid flock resulting therefrom into an aqueous dispersion as described later on which can be used in the formation of water insoluble films, webs and sheets, as a coating or adhesive composition and also for dispersion, stabilization and viscosity adjustment in paints, pigments, and inks.

We have found that cellulose glycolic acid can be precipitated from an aqueous solution of a cellulose glycolate salt, by acidification, in the form of a highly hydrated gelatinous flock, which can be substantially freed of excess precipitating acid and salt by-product without appreciably altering its hydrated gelatinous character. We have also found that the resultant hydrated gelatinous cellulose glycolic acid flock can be readily homogenized or dispersed with or without additional water or additives to form a uniform, stable, smooth, gelatinous dispersion having a creamy or paste-like character. This hydrated gelatinous dispersion can then be formed, as desired, into colorless, transparent, self-supporting, continous sheets and webs and used as coatings, sizings, and adhesives, which after drying, are completely water insoluble, are no longer capable of being rehydrated or swelled to any appreciable extent by water and therefore cannot be redispersed in water.

According to our invention, any soluble salt of cellulose glycolic acid can be employed for precipitating the gelatinous cellulose glycolic acid. For example, the alkali metal salts, such as the sodium, potassium and lithium salts, and the ammonium salt, form aqueous solutions suitable for this process. It is preferred to use the sodium salt since it is available on the market in low, medium and high viscosity grades and also in several degrees of glycolic acid substitution per anhydroglucose unit.

Strong acids, such as chloro-acetic acid, hydrochloric acid or sulfuric acid, are preferred in the acidification step to obtain a pH of 1 to 2 or lower for complete precipitation of the cellulose glycolic acid flock. A considerable excess of precipitating acid is desirable to obtain the gelatinous flock of cellulose glycolic acid in a firm compact form which will withstand the subsequent purification step. The precipitating acid can be poured into the solution of cellulose glycolate salt or the glycolate salt solution may be poured into the acid bath. We have found it advantageous to extrude the cellulose glycolate salt solution through an orifice, for example 1/16" or 1/4" in diameter, into an acid bath. With this technique, the cellulose glycolic acid is obtained in the form of insoluble, gelatinous, continuous, spaghetti-like rods or ropes which are shapes

US 3,403,093

well adapted to purification from excess acid and salt by-product.

Time of acidification or contact with the acid bath is not critical as long as the mineral acid has had sufficient time to diffuse thoroughly and uniformly through viscous cellulose glycolate salt solution. With the extrusion technique, using a 1/16" diameter orifice, 15 minutes' acidification time has been found adequate for penetration through the thin spaghetti-like rod of cellulose glycolate salt solution. With rods from larger diameter orifices, such as 1/4", requiring deeper penetration of the acid to accomplish acidification, a period of time as long as four hours may be required, depending, obviously, upon concentration of glycolate solution, concentration of acid and temperature.

Purification of the gelatinous cellulose glycolic acid flock of excess precipitating acid and salt by-product, for example, sodium sulfate or sodium chloride, can be accomplished by several well-known methods. For example, the gelatinous insoluble cellulose glycolic acid flock may be freed from an excess of impurities by diffusion washing in a continuous stream of water. We have found, for example, that gelatinous cellulose glycolic acid in the form of a spaghetti-like rod of 1/16" diameter can be substantially purified of much of the excess sulfuric acid and sodium sulfate by-product by diffusion washing in twenty minutes. In the case of spaghetti-like rods 1/4" in diameter, the time is longer, good results being obtained in approximately two to three hours. Samples of rods or ropes removed during the course of washing and then dispersed in a Waring Blender and then diluted to a definite concentration of cellulose glycolic acid, give colloidal solutions whose viscosity increases as washing progresses and as the precipitating agent and salts are removed.

The purified gelatinous cellulose glycolic acid flock can be homogenized or dispersed to a uniform, stable, smooth, gelatinous, creamy, viscous dispersion or sol by a variety of beaters, agitators and high speed mixers well known in the art, such as colloid mills, ball mills, homogenizers, and Oakes mixers. The viscosity of the resulting dispersion, at any given concentration, can be adjusted within an extremely wide range to obtain almost any desired final viscosity. For example, the viscosity may be raised by increasing the pH such as by the addition of very small amounts of basic materials, e.g., sodium hydroxide, but not in such amounts that a soluble glycolic acid salt is again formed. The viscosity may be lowered by decreasing the pH, such as by the addition of very small amounts of acids. Also, the addition of very small quantities of soluble salts such as aluminum chloride or sodium sulfate, acts to reduce the viscosity. If the washed and drained cellulose glycolic acid rods are permitted to stand for some time, e.g., four hours, before dispersion in a colloid mill, a higher viscosity results. Also, permitting the final dispersion itself to stand for several days at room temperature results in a slight increase in viscosity.

The cellulose glycolic acid dispersion or sol prepared in the above manner can be used as a coating or sizing agent, as an adhesive or for other purposes, such as a stabilizer for dispersions, and a viscosity modifier in paints, pigments or inks, or it can be converted into films and sheets. If the dispersion is to be converted into sheets, this can be done by any suitable well known type of film forming machine, such as a casting roller, to the surface of which the dispersion is applied, or by spraying upon the surface of an endless belt, followed by drying and some baking if a high degree of wet strength is desired. The resulting dry, self-supporting, continuous sheet may then be removed from the belt by a doctor knife and reeled or cut into sheets. The resulting sheet or film is transparent, flexible, water insoluble, and cannot be redispersed in water.

While the strength of films, coatings and sizings, formed from the dispersion described, is good, it is preferred to add a small quantity of an inert and tasteless filler to the dispersion before its use in producing the final desired product. Material such as kaolin, Bentonite, and Fuller's Earth, have produced satisfactory results in increasing the tensile strength of films, coatings and sizings. Aldehydes, such as glyoxal, and salts of certain trivalent and divalent cations such as aluminum chloride, which probably act to form cross linkages and increase the tensile strength in the final product, may also be used. Where better flexibility and prevention of brittleness are desired, it is preferred to add to the dispersion humectants and or plasticizers. Glycerine is a suitable humectant and is well adapted to the method because it also acts as a plasticizer. Obviously, other humectants, such as sorbitol, and ethylene glycol, may be used. The same obtains with respect to other well known types of plasticizers.

One use to which the novel film forming dispersion of the invention can be put is that of forming sheets of reconstituted tobacco wherein it is necessary to insure that the resulting product will have no deleterious effect on the smoking taste of the reconstituted tobacco produced, and the product must have a degree of resistance to steam, moisture and the saliva in the smoker's mouth. A reconstituted tobacco sheet of film, made with the aqueous cellulose gly-

GB 698,948

Source: https://www.industrydocuments.ucsf.edu/docs/xjnx0000

colic acid dispersion of this invention has these desirable properties. Films produced in accordance with our invention have adequate physical strength and water insolubility.

As noted hereinabove, dispersions of cellulose glycolic acid, made in accordance with the invention can be used satisfactorily as adhesives, especially where a water insoluble adhesive is desirable, as in sealing the longitudinal seam of the paper on a cigarette. Dispersions containing between 1.5 and 2.5% cellulose glycolic acid have proven satisfactory for this purpose, although this range may be varied to suit conditions of use.

The following examples will serve to illustrate our invention in further detail:

EXAMPLE 1

One liter of a solution of 3.75% (high viscosity grade, and 0.70 glycolic acid substitution per 1 anhydroglucose unit) sodium cellulose glycolate was prepared and extruded in the form of a continuous spaghetti-like rod approximately 1/16" diameter into a bath of 4 liters of 22% sulfuric acid and allowed to stand for 20 minutes, during which time the acid penetrated the sodium cellulose glycolate rod to form the gelatinous cellulose glycolic acid. The insoluble spaghetti-like cellulose glycolic acid in the form of gelatinous rods was then removed from the acid bath and washed for 90 minutes in a water bath at a continuous water flow of approximately 5 gallons per minute at a water temperature of 70 F. The washed spaghetti-like rods, substantially free of excess sulfuric acid and sodium sulfate, were removed, drained and colliod milled. The resulting dispersion contained approximately 0.8% cellulose glycolic acid.

EXAMPLE 2

One liter of 4% solution of sodium cellulose glycolate (same type as in Example 1) was prepared and extruded in the form of a continuous rod approximately 1/16 inch in diameter into a bath of 2 liters of 20% hydrochloric acid and allowed to stand for 5 minutes, during which time the hydrochloric acid penetrated the sodium cellulose glycolate and converted it to cellulose glycolic acid. The insoluble spaghetti-like gelatinous cellulose glycolic acid was then removed from the acid bath and washed for 30 minutes in a water bath at a continuous water flow of approximately 5 gallons per minute at a water temperature of 70 F. The washed product was removed, drained, and dispersed in an Oakes Mixer, a type of high speed rotary mixer having a stator and a rotor and means for forcing the material being processed into the range of the stator and rotor. The resulting dispersion contained approximately 2.5% cellulose glycolic acid.

EXAMPLE 3

Same as Example 1, except that 0.4% of kaolin and 0.8% of glycerine, based on the total weight of the finished dispersion, were added to the dispersion after colloid milling and the mixture passed again through a colloid mill to incorporate these additives and form a uniform product.

EXAMPLE 4

Same as Example 1, except that 0.27 grams of a 30% solution of glyoxal in water was added to 100 grams of the finished dispersion after colloid milling, and the mixture was passed again through a colloid mill to form a uniform product.

EXAMPLE 5

One liter of 2.5% solution of sodium cellulose glycolate (medium viscosity grade, containing approximately 0.35 glycolic acid substitution per 1 anhydroglucose unit) was extruded in the form of a continuous rod approximately 1/4 inch in diameter into a bath of 3 liters of 25% sulfuric acid and allowed to stand for 4 hours. The resultant insoluble gelatinous cellulose glycolic acid in the form of spaghetti-like "noodles" was washed, as in Example 1, for three hours. The substantially pure cellulose glycolic acid was processed in a Waring Blender for 2 minutes. The resulting dispersion contained approximately 1.8% cellulose glycolic acid.

EXAMPLE 6

The same as example 4, except that 0.9% of kaolin and 1.8% of glycerine, based on the weight of the finished dispersion in Example 4, were added to the final dispersion and the mixture agitated violently in a Waring Blender to disperse these additives uniformly.

The dispersions produced in accordance with the invention, and as exemplified in the above examples, are suitable for use in coatings and sizings as described hereinabove, and also may be formed directly into self-supporting webs and films. When made into webs and films, a preferred method is to cast the dispersion as a thin, continuous web on a film forming surface, such as an endless travelling stainless steel belt. After casting, the film or web is dried and removed by a suitable device such a doctor blade, well known in the art, in the form of a continuous self-supporting insoluble cellulose glycolic acid web.

In the desesription hereinabove, reference has been made to the use of cellulose glycolic acid and its conversion into stable insoluble aqueous dispersions. The invention is also concerned with the half ethers of cellulose glycolic acid with ethylene glycol known in the art as carboxymethyl hydroxyethyl cellulose, these ethers being available in various degress of substitution per anhydro glucose unit both with respect

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

to the ratio of glycolic acid substitution per such unit and the ratio of ethylene glycol half ether substitution per anhydro glucose unit or various comonifications of both these ratios. In general, the techniques described hereinabove for forming aqueous dispersions of cellulose glycolic acid are followed in making aqueous insoluble dispersions of carboxymethyl hydroxyethyl cellulose, which is a material having substantially the same characteristics for the purpose of our invention as cellulose glycolic acid. A satisfactory dispersion of carboxymethyl hydroxyethyl cellulose for use in forming insoluble films, webs and sheets, and also in sizings and coatings, in substantially the same manner as above described dispersions of cellulose glycolic acid can be made as follows:

EXAMPLE 7

Four and one-tenth grams of the dry sodium salt of carboxymethyl hydroxyethyl cellulose were dissolved in sufficient water to form a thick paste. The paste was extruded through a 1/16 inch diameter orifice into 20% sulfuric acid solution and permitted to stand in the acid for two hours. The resulting hardened spaghetti-like threads of insoluble carboxymethyl hydroxyethyl cellulose were removed from the acid, drained, and washed with running water for 20 minutes. The washed threads were then dispersed into a stable aqueous dispersion by processing in a Waring Blender, and the dispersion was cast into a wet web on a plate. The web was dried and the film stripped from the plate. The film was insoluble in water.

We are aware of the Tobacco Act, 1842 (5 and 6 Vict. Cap 93) and make no claim to the use of this invention in contravention of any provisions of that Act. We do, however, expressly make claim to any use of the invention which may now be in contravention of the said Act and which may hereinafter become legal as a result of modification or repeal of the said Act as of the date such use becomes legal.

What we claim is:—

1. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose which comprises acidifying an aqueous solution of a soluble cellulose glycolate salt or soluble salt of carboxymethyl hydroxyethyl cellulose to precipitate gelatinous, cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose flock therefrom, separating said flock from said acidified solution, washing said flock, and dispersing (as hereinbefore described) said flock in water to form said dispersions.

2. Method as claimed in Claim 1 in which the gelatinous flock is dispersed by agitating the flock in water.

3. Method as claimed in Claim 1 and in which the gelatinous flock is dispersed by grinding.

4. Method as claimed in Claim 1, 2 or 3 in which an aqueous viscous solution of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose is extruded into an acid bath to produce ribbons or rods of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose, said ribbons or rods being converted by said acid into gelatinous ribbons or rods of cellulose glycolic acid, or carboxymethyl hydroxyethyl cellulose, which are then separated, washed and dispersed in water.

5. Method as claimed in any of the preceding claims in which a small amount of a filler is added to the so produced dispersion.

6. Method as claimed in Claim 5 in which the filler is kaolin.

7. Method as claimed in any of the preceding claims in which a small quantity of a humectant is added to the so produced dispersion.

8. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose substantially as described with reference to the examples.

9. Webs and films from dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose obtained in accordance with the preceding claims which are made by casting the dispersions into a continuous web or film from which moisture is removed to make it self-supporting.

10. A dispersion of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose whenever obtained by the method claimed in any of Claims 1 to 8.

MARKS & CLERK.

Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4.—30/244—1953.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

Source: https://www.industrydocuments.ucsf.edu/docs/xpnx0000

to the ratio of glycolic acid substitution per such unit and the ratio of ethylene glycol half ether substitution per anhydro glucose unit or various comoinations of both these ratios. In general, the techniques described hereinabove for forming aqueous dispersions of cellulose glycolic acid are followed in making aqueous insoluble dispersions of carboxymethyl hydroxyethyl cellulose, which is a material having substantially the same characteristics for the purpose of our invention as cellulose glycolic acid. A satisfactory dispersion of carboxymethyl hydroxyethyl cellulose for use in forming insoluble films, webs and sheets, and also in sizings and coatings, in substantially the same manner as above described dispersions of cellulose glycolic acid can be made as follows:

EXAMPLE 7

Four and one-tenth grams of the dry sodium salt of carboxymethyl hydroxyethyl cellulose were dissolved in sufficient water to form a thick paste. The paste was extruded through a 1/16 inch diameter orifice into 20% sulfuric acid solution and permitted to stand in the acid for two hours. The resulting hardened spaghetti-like threads of insoluble carboxymethyl hydroxyethyl cellulose were removed from the acid, drained, and washed with running water for 20 minutes. The washed threads were then dispersed into a stable aqueous dispersion by processing in a Waring Blender, and the dispersion was cast into a wet web on a plate. The web was dried and the film stripped from the plate. The film was insoluble in water.

We are aware of the Tobacco Act, 1842 (5 and 6 Vict. Cap 93) and make no claim to the use of this invention in contravention of any provisions of that Act. We do, however, expressly make claim to any use of the invention which may now be in contravention of the said Act and which may hereinafter become legal as a result of modification or repeal of the said Act as of the date such use becomes legal.

What we claim is:—

1. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose which comprises acidifying an aqueous solution of a soluble cellulose glycolate salt or soluble salt of carboxymethyl hydroxyethyl cellulose to precipitate gelatinous, cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose flock therefrom, separating said flock from said acidified solution, washing said flock, and dispersing (as hereinbefore described) said flock in water to form said dispersions.

2. Method as claimed in Claim 1 in which the gelatinous flock is dispersed by agitating the flock in water.

3. Method as claimed in Claim 1 and in which the gelatinous flock is dispersed by grinding.

4. Method as claimed in Claim 1, 2 or 3 in which an aqueous viscous solution of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose is extruded into an acid bath to produce ribbons or rods of sodium cellulose glycolate or the sodium salt of carboxymethyl hydroxyethyl cellulose, said ribbons or rods being converted by said acid into gelatinous ribbons or rods of cellulose glycolic acid, or carboxymethyl hydroxyethyl cellulose, which are then separated, washed and dispersed in water.

5. Method as claimed in any of the preceding claims in which a small amount of a filler is added to the so produced dispersion.

6. Method as claimed in Claim 5 in which the filler is kaolin.

7. Method as claimed in any of the preceding claims in which a small quantity of a humectant is added to the so produced dispersion.

8. Method of forming aqueous dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose substantially as described with reference to the examples.

9. Webs and films from dispersions of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose obtained in accordance with the preceding claims which are made by casting the dispersions into a continuous web or film from which moisture is removed to make it self-supporting.

10. A dispersion of cellulose glycolic acid or carboxymethyl hydroxyethyl cellulose whenever obtained by the method claimed in any of Claims 1 to 8.

MARKS & CLERK.

Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 39/244—1953.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

000037097

and light conditions. The colored complex seems more stable than the α-TNT, and it is difficult to reverse the reaction, once the colored complex is formed. All water samples containing colored TNT must be examined for TNT in both forms. α-TNT solutions in tap waters of low alkalinity or polluted waters will remain uncolored for 100 days and longer in the dark at 20° C. α-TNT solutions in distilled water can be exposed to sunlight for long periods with the formation of only a trace of colored complex and without other decomposition. With relatively pure or polluted surface waters, from 40 to 55% of α-TNT is converted to the colored form in 80 days at ordinary temperatures in intermittent sunlight. The percentage of colored TNT formed can be increased to 90% or more in one day or less by increasing the alkaline constituents of the water and/or the temperature.

The conversion of α-TNT to the colored form is considered the principal reaction during prolonged storage of TNT solutions. During this conversion, however, there is a slow reduction of total TNT which depends to a large extent upon carbonate concentration or pH and light conditions. In the surface and polluted water samples tested, 65 to 75% of the original TNT remained in one form or the other after 80 days in intermittent sunlight. In water containing 300 to 1000 p.p.m. of normal carbonate, 53 to 55% of the TNT remained (largely in the colored form) after 36 days in intermittent sunlight. This decomposition reaction is considered too slow for practical application.

Concentrations of α-TNT above 1.0 p.p.m. have a retarding effect on the biochemical oxidation of sewage. There is little biochemical removal of TNT as the result of biochemical oxidation in dilute sewage. Colored TNT was equally as inhibitive as α-TNT to normal biochemical oxidation of organic matter during the carbonaceous stage. The study of colored TNT wastes indicated that no reduction of the color can be expected by natural biochemical purification in streams.

Raw domestic sewage at pH values of 7.2 to 7.8 removed concentrations of α-TNT up to about 35 p.p.m. from solution in a 24-hour contact period. The quantity of TNT removed seems to depend upon the suspended organic matter in the sewage. The rate of anaerobic digestion of sewage solids is decreased considerably by the TNT absorbed. It was more difficult to remove colored TNT from solution during primary treatment of sewage than α-TNT.

Even with concentrations of α-TNT as low as 30 p.p.m. in sewage, activated sludge treatment requires aeration periods up to 24 hours for 90% removal of both TNT and B.O.D. Although colored TNT did not inhibit the process as much as alpha, it was not removed so readily.

Filtration experiments indicated that a black garden soil was best for removing TNT. Such soils might be expected to remove a total amount of TNT up to about 0.1% of their weight. Colored TNT is removed more effectively by all soils than α-TNT. Alkalinizing the waste slightly with soda ash to convert the TNT to the colored form is advantageous for soil percolation. As the absorption capacity of the soil becomes exhausted, fresh water removes some of the absorbed TNT.

Dosing and mixing activated carbon into the waste were more effective in removing TNT than filtration through carbon. α-TNT was removed from solution more readily than the colored derivative. A satisfactory chemical treatment of TNT wastes from shell-loading plants would involve holding the TNT in the alpha form, followed by treatment with activated carbon to remove it from solution. Such a procedure is considered practical for the volumes of waste discharged from shell-loading plants.

LITERATURE CITED

(1) Ruchhoft, C. C., *Sewage Works J.*, 13, 669 (1941).
(2) Ruchhoft, C. C., and Meckler, W. G., IND. ENG. CHEM., ANAL. ED., 17, 430 (1945).
(3) Schott, Stuart, Ruchhoft, C. C., and Megregian, Stephen, IND. ENG. CHEM., 35, 1122 (1943).

PRESENTED as part of the Symposium on Industrial Wastes before the Division of Water, Sewage, and Sanitation Chemistry at the 108th Meeting of the AMERICAN CHEMICAL SOCIETY in New York, N. Y.

CARBOXYMETHYLCELLULOSE ····

Uses and Applications

C. B. HOLLABAUGH, LELAND H. BURT, AND ANNA PETERSON WALSH

Hercules Powder Company, Wilmington, Del.

THE newest member of the cellulose derivative family to be introduced commercially, carboxymethylcellulose, is finding wide acceptance in industry. It is the reaction product of monochloroacetic acid on alkali cellulose, and is generally supplied to the trade as the sodium salt which is a white, granular, odorless, and tasteless powder. This salt is readily soluble or dispersible in water or alkaline solutions to form highly viscous solutions useful for their thickening, suspending, and stabilizing properties; furthermore, these solutions can be evaporated to form tough films.

The sodium salt of carboxymethylcellulose is known in the trade by several different names including cellulose gum, sodium cellulose glycolate, Carboxymethocel, Collocel, and CMC. The first two are used as general trade designations; the last three are trade names for specific types sold by individual producers.

A reasonably complete summary of published literature (both patents and technical articles) on carboxymethylcellulose and its derivatives is assembled here. No effort has been made to evaluate the literature references, because commercial exploitation of carboxymethylcellulose is so recent and is expanding at such a rate that any critical evaluation could be out of date before publication. Research in this laboratory has been carried out on possible useful applications of the product. Conclusions not yet published are cited throughout this paper without literature references; they are for the reader's use in conjunction with his study of the references cited.

Since it was first developed by Jansen (*40*) in Germany toward the end of World War I, carboxymethylcellulose has been suggested as a substitute for such products as gelatin, glue, gum arabic, agar-agar, carragheen moss, tragacanth, cherry gum, wheat gluten, and locust bean gum (*33, 40*). The original Jansen process was later improved upon by Chowdhury (*6*) and Höppler (*33*).

Carboxymethylcellulose is usually used in the form of its sodium salt (cellulose gum) which, so far, is its most important industrial derivative (*3*). Low-substituted types, soluble in alkali but not in water (*20, 50*), are known. A highly substituted form (*10*), insoluble in alkali or water but soluble in organic solvents, has also been produced. The potassium salt resembles the sodium salt in many of its properties and gives a similar solution in water. The ammonium salt also is water soluble, and is particularly interesting because it is unstable and loses ammonia on heating to 50–60° C. The chief insoluble salts of carboxymethylcellulose so far investigated are those of lead, silver, mercury, and aluminum, all of which are colorless, the copper and nickel salts which are blue, and the ferric salt which is red.

Generally speaking, sodium carboxymethylcellulose is indicated wherever hydrophilic colloids possessing marked suspending,

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

thickening, stabilizing, and film-forming properties are required. Some of the better-known applications cited are as thickening agents in textile print pastes and as textile finishing and sizing agents (*33*). Sodium carboxymethylcellulose can be used as an emulsifying agent. Also, it is applicable wherever a protective colloid is needed in oil-in-water emulsions (*5*). Its excellent film-forming properties should be valuable in paper sizing and coating. Höppler (*33*) disclosed the use of sodium carboxymethylcellulose in adhesives, color agglutinants, emulsifying agents, finishing and sizing agents, low-viscosity material to be used for textile finishes and sizes (the medium- and high-viscosity materials were disclosed for use as color agglutinants), paper-hanging paste, thickeners, and emulsifying agents. Feeding tests (*5*) on animals showed it to be harmless physiologically.

Commercial usage of carboxymethylcellulose, usually in the form of its sodium salt, has increased rapidly in recent years. This product is a cellulose derivative formed by the reaction of monochloroacetic acid on alkali cellulose. The sodium salt is readily soluble or dispersible in water to form highly viscous solutions. Such solutions are utilized for their thickening properties, to aid in the suspension of pigments and other finely divided solids in liquid media, and to stabilize emulsions of various types. This article discusses briefly and gives references to most of the published literature without effort to evaluate the many and varied suggestions. Most of the references in the appended bibliography show publication dates of recent years.

TEXTILE INDUSTRY

In the textile industry many uses based on the high-viscosity and film-forming properties of sodium carboxymethylcellulose have been proposed. This water-soluble product has been suggested for use in printing pastes, sizes, finishes, and lubricants. Allan and Wainwright (*1*) disclosed its application as an aqueous printing paste for use on cellulose-derivative fabrics such as those from cellulose acetate. The paste contained a high-boiling solvent for the fabric material, a coloring material, water, and, as a thickening agent, enough water-soluble carboxymethylcellulose to give a 5% aqueous solution having a specific viscosity of 20 centipoises (capillary tube method). Johnson (*41*) used less than 1% of the sodium salt of carboxymethylcellulose to stabilize dye suspensions, and to prevent settling and froth or foam formation upon storage. Sodium carboxymethylcellulose treated with epichlorohydrin to increase its viscosity was reported as being useful in printing pastes for textiles (*58*). Oxley and co-workers suggested the use of carboxymethylcellulose for printing pastes (*71*). In order to increase dye penetrations in fabric coloring, the wetting property of the sodium salt was utilized (*23*). Also, this wetting property was said to be useful for promoting bleeding or running in the dyeing of piece goods (*37*). Sodium carboxymethylcellulose has also been suggested (*7*) as a retardant in vat dyeing of textiles.

Sponsel (*32*) discussed the use of water-soluble carboxymethylcellulose in sizes and in water-soluble finishing agents; it was considered particularly valuable for wool sizing on account of its good film-forming properties. In finishing operations, the stability of carboxymethylcellulose toward the effects of light, temperature, and bacteria were said to be very good. This investigator reported that the water-soluble carboxymethylcellulose can be mixed and used together with not only the older known starches and usual fatty substances but also with such synthetic substances as acrylic acid esters and polyvinyl ethers. A gas-retaining fabric was prepared (*39*) by coating a base fabric with an aqueous solution of a soluble salt of carboxymethylcellulose and insolubilizing it with acetic acid.

Dreyfus and co-workers disclosed the warp sizing of yarns with aqueous solutions or dispersions of carboxymethylcellulose (*18*), as well as the use of these solutions in the sizing of filaments, threads, yarns, fabrics, and other textile material (*19*). Dreyfus (*15*) employed aqueous solutions of an ammonium salt of carboxymethylcellulose for sizing textile yarns, and Roberts described for the same purpose the use of the aluminum salt which is insoluble in water (*78*). A water-soluble carboxymethylcellulose powder prepared by drying an aqueous solution in thin films at above 100° C. has been proposed for use in various ways and as a thickener for printing inks (*67*). A glazed finish for fabrics was reported as having been obtained by applying carboxymethylcellulose and a reactive decomposable quaternary ammonium salt, drying, calendering, and at some stage reacting the carboxymethylcellulose and the ammonium compound by heating to yield an insoluble coating (*36*). Films of water-soluble carboxymethylcellulose can be used for sizing dairy filter cloth.

Brown and Houghton revealed that sodium carboxymethylcellulose acts as an effective stabilizer for oil emulsions; they used 0.5 to 1%, preferably of the high-viscosity type with such oils as castor, linseed, rapeseed, and liquid paraffin in conjunction with sodium stearate and members of the olive oil series.

In the field of textile finishing, the water-insoluble alkali-soluble type of carboxymethylcellulose was said by Sponsel (*32*) to be important because of the permanence of the finish which could be obtained. He stated that twenty-five washings of fabrics treated with an alkali-soluble cellulose ether did not remove the ether from the fabric. Since the alkali-soluble cellulose derivative may be applicable to cotton goods, denims, and linenlike cotton white goods, the principal field for it was thought to be in cellulose wool, artificial silk, and mixed fabrics. The finishing agent also was said to allow production of a plastic effect on velvet, clothing, and furniture fabrics. Lilienfeld (*50*) advocated the use of the alkali-soluble carboxymethylcellulose in textile finishing and disclosed a process in which cotton or other woven fabrics were coated with one or several layers of carboxymethylcellulose, dried between coats, steamed after the last coat, passed through a precipitating bath, washed and dried, all under tension. The precipitating or coagulating medium for a permanent size of alkali-soluble carboxymethylcellulose was reported to be a 10% sulfuric acid solution (*20*). Brown and Cooper (*2*) utilized the material as a laminating layer for fabrics. Using the type of carboxymethylcellulose which is soluble in alkali at low temperatures only, Bolton (*2*) sized cotton fabrics with a caustic soda solution of the carboxymethylcellulose and coagulated the carboxymethylcellulose on the fabric with 5% sulfuric acid followed by 5% alum solution.

The alkali-soluble carboxymethylcellulose has been reported as being useful in printing pastes. According to Lilienfeld (*50*), 100 parts of carboxymethylcellulose, 6 to 10 parts of mica or 4 parts of lampblack or 8 to 10 parts of zinc oxide can be printed with suitable printing rollers on cotton materials. The printed fabric in the dry condition is then treated with a precipitating solution to set the layer. Houghton and Craik (*34*) treated

0000331099

Source: http://www.industrydocuments.ucsf.edu/docs/xpmx0000

solution of carboxymethylcellulose in dilute aqueous alkali with a coagulating agent so as to produce gelatinous properties without complete gelation or precipitation, and used this dispersion with pigments on textiles. Clark (6) showed that alkali-soluble carboxymethylcellulose is a carrier for those dyestuffs which are developed after their application to textile material.

Alkali-soluble carboxymethylcellulose after heat treatment at 40° C. for 12 to 24 hours plus treatment at 250° C. for 5 minutes may be used, according to Lilienfeld (57), for fabric dressings, textile printing pastes, book cloth, tracing cloth, and yarn sizing. Lilienfeld (49) partially reacted cellulose in the form of fabrics with monochloroacetic acid in the presence of an alkali at 50° to 60° C. until the effect desired was obtained. It was claimed that patterns and differential printing effects could be produced in this way. Dreyfus elaborated on this textile treatment (14). Textile fabrics of carboxymethylcellulose were stabilized by treatment with 0.25 to 5.0% of a soluble thiocyanate (55).

PAPER INDUSTRY

Carboxymethylcellulose has been proposed for sizing and coating compositions, and for use in pulp impregnants. Thomas and Oxley (85) disclosed the use of boric-acid-treated carboxymethylcellulose as a size for paper. The grease-resistant properties of carboxymethylcellulose suggested that it might be especially valuable in greaseproofing paper. Merrill (65) disclosed it as both a beater size and a surface size for greaseproof paper, useful for packaging foodstuffs. He claimed that such sizes also could be used to control printing ink penetration. Wrapping paper for dynamite cartridges, sized with carboxymethylcellulose, was said to have a lower rate of vapor diffusion for volatile explosive constituents such as ethylene glycol dinitrate.

To a beater furnish, Larson (48) added a 1% solution of carboxymethylcellulose which was then precipitated with alum. This furnish was then sheeted and treated with an alkaline agent to render the size highly swollen to just short of a sol state. The action of the swelling agent was stopped at that point, and the sheet dried in the usual manner, to give a grease-resistant paper suitable for packaging foodstuffs and lubricating oil.

Paper coatings of carboxymethylcellulose and its sodium salt were described by Gloor (27) who combined 10 parts of carboxymethylcellulose with 2 to 30 parts of an alkali metal silicate, such as water glass, to coat or impregnate paper or fiberboard. Kallock (42) used carboxymethylcellulose in a blushing lacquer for paper to give a pressure-sensitive chart paper.

The alkali-soluble water-insoluble carboxymethylcellulose was first disclosed for use as a paper size and coating by Lilienfeld (50). An example of sizing with this type was given by Maxwell and Larson (60) in which a sodium carboxymethylcellulose was added to a clay coating composition. The binding effect given by one third as much carboxymethylcellulose as had been previously used of casein was said to be equivalent to that obtained with a good grade of casein. Dilute, aqueous, colloidal solutions of the salts of carboxymethylcellulose were claimed to be suitable for sizing colored paper (80). Krestinskii (46) found alkali-soluble carboxymethylcellulose useful in the impregnation of pulp for waterproofing. Freeman, Peterson, and Greminger (25) disclosed a greaseproofed paper treated with an ammoniacal solution of aluminum carboxymethylcellulose. Roberts (78) reported aqueous aluminum carboxymethylcellulose solutions for sizing paper, and Sichel (81) also showed viscous solutions of the aluminum salt to be useful as size.

FOOD INDUSTRY

Tests were carried out by Brown and Houghton (5) in England and Werle (91) in Germany to establish the fact that sodium carboxymethylcellulose is physiologically inert. The chemical constitution suggested to them that it should be innocuous, and [illegible] indicated that rats and dogs suffered no ill effects. Post mortem examination of the vital organs showed these to be normal in every way. An analysis (5) of the foodstuff quality of one variety of carboxymethylcellulose showed the lead content of the salt to be only 8 parts per million, and copper and zinc were each less than 1 p.p.m. It was concluded, therefore, that it could be used in preparations for internal consumption such as medicine and foodstuffs as well as in toilet preparations for external application (5, 91).

Maxwell (58) disclosed that carboxymethylcellulose treated with epichlorohydrin could serve as a thickener for food, and Wallach (89) claimed that the addition of 10 to 50% water-soluble carboxymethylcellulose, based on the weight of pure carbohydrate or carbohydrate foodstuffs would reduce the absorbability of such foods. The alkali-soluble carboxymethylcellulose may be used, it is said (9), to stabilize salts of hydrosulfurous acid and related hydrosulfite compounds toward moist air, particularly where the hydrosulfite product is used in an alkaline bath. These stabilized hydrosulfite compounds were disclosed for bleaching fats and sugar (9).

The water-soluble salts of carboxymethylcellulose, particularly sodium carboxymethylcellulose, are being used to stabilize ice cream, sherberts, and ices, as well as chocolate milk and some types of cheese. They can be used in place of gums in icings, meringue powders, doughs, flours, jellies, pie fillings, puddings, and other bakery products. Their effective function as a protective colloid is used in oil-in-water emulsions such as flavor emulsions, salad dressing, and some types of mayonnaise.

Reichel (76) and co-workers suggested the preparation of sausage casings from carboxymethylcellulose followed by conversion of the carboxymethylcellulose to cellulose hydrate. Such casings also have been prepared by extruding a mixture of alkali-soluble carboxymethylcellulose and cellulose xanthate in alkaline solution and coagulating the mixture, followed by reconversion of the xanthate to cellulose hydrate (74).

A film of carboxymethylcellulose is reported as having found use as a flexible wrapper for frozen foodstuffs (76). Greasy or oily foods may be packaged in paper containers coated with water-soluble carboxymethylcellulose according to Collings, Peterson, and Kelly (8).

DRUGS AND COSMETICS

One investigator reported that sodium carboxymethylcellulose may be used to replace tragacanth, carob gum, and gum arabic in the manufacture of face creams, and may be used as a base or stabilizer in medicinal preparations (43). According to Wenck (90), it may be employed with agar-agar as a medium for cultivating bacteria. Hiatt (32) reported that medicaments, such as capsules, tablets, and powders surrounded by an enteric film or layer of carboxymethylcellulose, are insoluble in the stomach acids but soluble in alkaline intestinal fluids. Development of liquid-absorbing surgical dressings saturated with water-soluble carboxymethylcellulose have been reported (63).

Protective colloid action of the water-soluble salts of carboxymethylcellulose has found application in dentifrices, wave set compositions, hand lotions, and other types of pharmaceutical and cosmetic emulsions (62). Their ease of dispersion in hot or cold water makes them valuable as ointment bases in the drug field. Their grease and organic solvent-resistant films are useful in protective hand creams. Dental impression materials might contain various salts of carboxymethylcellulose.

Stains from copying inks or pencils or from typewriter ribbons, it is claimed, may be removed by compositions of pasty consistency containing carboxymethylcellulose swollen by water with or without the addition of soap or glycerol (58).

CERAMICS

Ceramic bodies, especially for electrical purposes, can be more readily manufactured by mixing with the ceramic material carboxymethylcellulose which swells or dissolves [illegible]

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

molding the ceramic body and sintering it at a temperature of about 1500° C. (70).

LEATHER

Lilienfeld (50) described in early patents the use of alkali-soluble water-insoluble carboxymethylcellulose as a leather dressing. This type can also be used, it is said, for impregnating leather to increase its waterproofness (46). A leather coating and coloring composition has been reported which contains 100 grams of a 5% solution of a carboxymethylcellulose salt, 3 grams of Turkey red oil, 2 grams of glycerol, 15 grams of dyestuff, and 30 grams of water (72). The water-soluble salts are being used to control adhesiveness in the leather-pasting operation.

PAINTS AND LACQUERS

Because of its film-forming properties, carboxymethylcellulose has been proposed for many types of protective coatings. Lilienfeld (50) disclosed coatings of the alkali-soluble type resistant to water and most chemicals; he also recommended a heat-treated carboxymethylcellulose for this purpose (57).

The water-soluble salts of carboxymethylcellulose have been suggested by Köhler (44) for the priming of interior walls, particularly when coloring matter is desired in the prime coat.

Medl (61) described an aqueous composition particularly suitable for coating iron and other surfaces; his composition contained sodium carboxymethylcellulose with water-soluble non-acid salts of phosphoric, boric, and other polybasic acids to prevent rusting by the solution. These coatings are said to be impervious to grease and oil. He also suggested (62) a complex ester condensation product of a polyhydric alcohol with boric acid as a modifier to plasticise films of carboxymethylcellulose which are used as coatings for paper, cardboard, plaster or concrete surfaces, iron structural members, and black iron sheets.

The epichlorohydrin-treated carboxymethylcellulose of Maxwell (58) was reported as a thickening agent in emulsion-type paints. Sodium carboxymethylcellulose was also suggested for emulsion paints and lacquers (69). Carboxymethylcellulose may be used, it is said, to extend white pigments and improve their hiding power in flat paint formulations (28, 29).

Reichel and Craver (77) reported carboxymethylcellulose as a hydrophilic colloid thickener in a coating composition containing a cellulose derivative and a wax in an organic solvent. The water-insoluble polyvalent metal salts of carboxymethylcellulose (26) also have been recommended for coatings.

Water-soluble salts of carboxymethylcellulose are being used to control viscosity and brushing properties, and to protect the emulsion in resin emulsion paints.

Slightly soluble crystalline materials, useful as pigments, extenders, fillers, or bases, such as calcium sulfate, may be treated, it is said, with water-soluble salts of carboxymethylcellulose to inhibit crystalline growth (85).

ADHESIVES

Voss (87) disclosed both the water-soluble and alkali-soluble types of carboxymethylcellulose as adhesives. A viscous aqueous solution containing 3 to 8% of sodium, potassium, ammonium, triethanolamine, or triethylammonium carboxymethylcellulose, alone or with soluble starches, was reported as forming adhesives suitable for hanging wallpaper or pasting paper products such as boxes (44). Robie (79) reported the use of carboxymethylcellulose to bond abrasive particles to a base in the manufacture of sandpaper and various abrasive articles.

The alkali-soluble type was proposed as an adhesive by Lilienfeld (50), Maxwell and Larson (60), and others. It has also been suggested as a cement for laminating nonfibrous sheets (88).

Meyer (67) disclosed a specially dried and powdered water-soluble carboxymethylcellulose or its sodium salt as an adhesive, and Medl (61) reported the use of a sodium carboxymethylcellulose with alkaline salts of phosphoric, boric, or other polybasic acid in adhesives.

The aluminum salt of carboxymethylcellulose as an adhesive for pasting paper and wallpaper was described by Sichel (81).

FILMS AND FILAMENTS

Films of carboxymethylcellulose, particularly the alkali-soluble type, have been proposed for "cellophane-type" wrappings. Such films are said to be tough and difficultly combustible (40).

Lilienfeld (50) disclosed films prepared by coagulating an alkaline solution of a water-insoluble carboxymethylcellulose with 10 to 20% sulfuric acid, 25% acetic acid, 30% ammonium chloride solution, 20% tannin, or 40% formaldehyde solution, or by the usual viscose precipitating bath. The solidified film was washed with water and dried. Flexibility may be increased, it was said, by plasticizing with 10% glycerol. Ellsworth (20, 21) coated alkali-soluble films of carboxymethylcellulose with a composition of a synthetic resin with wax and plasticiser to increase moisture resistance. A coating or surface size of nitrocellulose or other cellulose derivative emulsion may be used with water-sensitive films according to Kojevnikoff (45). In preparing a wrapping tissue of carboxymethylcellulose carrying a moistureproofing coating, Müller and Herrmann (68) used an intermediate coating of the polymerization product of maleic anhydride and vinyl methyl ether. For wrapping frozen foods, a carboxymethylcellulose film plasticized with water, glycerol, and diethylene glycol was recommended (75).

It is reported that alkali-soluble films of carboxymethylcellulose may be treated with deformation-restricting agents (63, 64, 86). A film of mixed structure (84) was prepared by precipitating 20 parts of a polyamide dissolved in 6 *N* hydrochloric acid in a bath consisting of a solution of 10 parts of carboxymethylcellulose in 80 parts of 6 *N* sodium hydroxide.

MISCELLANEOUS

Miscellaneous proposed uses of carboxymethylcellulose include a coating for the inside of metal molds used for the polymerization of resin-forming liquids (24), sticking agents for insecticides (60), clarifying agents for liquids (60), crystallization inhibitors (60), boiler compounds (31), creaming and thickening latex (31, 66, 80), oil drilling muds (31), can-sealing compounds (31), antistick compounds to prevent blocking, and emulsifiers in the photographic field (43). The water-soluble salts may also be used as suspending agents in tungsten wire-drawing compounds.

The molding of insulating blocks has been patented, using 1.5 to 5% of a polyvalent metal salt of carboxymethylcellulose as the binder for exfoliated vermiculite (73). The aluminum, copper, zinc, iron, tin, nickel, and chromium salts were said to be suitable.

Substances found to be compatible with carboxymethylcellulose, which may be used in conjunction with it, include hydrated cellulose or hydrocellulose soluble in alkalies; viscose (cellulose xanthate) in the crude form or purified by any known process; albuminous substances, proteins, and glue (gelatin); amylon, starch, and starchlike materials; tragasol; resins soluble in alkalies; resinous condensation products (soluble in alkalies) obtained by the condensation of a phenol or an aromatic amine or of a urea with an aldehyde; shellac; glycerol, diglycerol, polyglycerol, glycols, and sugars and sirups; soaps, fats, ammonium or alkali-metal derivatives of fatty sulfonic acids such as Turkey red oil (50); drying or nondrying oils; and halogen derivatives of polyhydric alcohols, particularly halohydrins (67).

Carboxymethylcellulose, it is said, may be plasticised with polyhydric alcohols (47) or special *N*-hydroxyalkyl amides (96). Aluminum carboxymethylcellulose in combination with wax in an ammoniacal solution has been disclosed (94).

Since carboxymethylcellulose was first developed during World War I as a substitute for scarce natural products, it has

0000331101

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

attained a position based on its own virtues. Unique among cellulose derivatives, it acts both as a film former and as a stabilizer and emulsifier for aqueous systems. This combination of properties makes carboxymethylcellulose potentially useful in fields in which gums, glues, and gelatins have so far not been used.

Neither the highly substituted organic-soluble type of carboxymethylcellulose (*10*) nor its many derivatives, with the exception of the metallic salts, have been discussed in this paper. The numerous possibilities for derivatives are illustrated in part in patents which show xanthate derivatives (*22, 51, 53, 54, 55*); nitrogen-containing derivatives (*11, 16*); acid halides of carboxymethylcellulose (*12, 13*); derivatives containing carboxy and amine groups (*17*); and mixed ethers (*56*). Mixtures of carboxymethylcellulose with viscose have also been suggested (*58, 59*).

LITERATURE CITED

(1) Allan, J., and Wainwright, J. A. (to Celanese Corp.), U. S. Patent 2,248,048 (July 8, 1941).
(2) Bolton, E. K. (to Du Pont Co.), *Ibid.*, 2,087,237 (July 20, 1937).
(3) Brown, C. J., and Houghton, A. A., *J. Soc. Chem. Ind.*, 60, 254–8 (1941).
(4) Brown, R. R. H., and Cooper, J. N. (to Imperial Chem. Ind.), U. S. Patent 2,192,297 (March 5, 1940).
(5) Chowdhury, J. K., *Biochem. Z.*, 148, 76–97 (1924).
(6) Clark, J. A. (to Sylvania Industrial Corp.), U. S. Patent 2,259,796 (Oct. 21, 1941).
(7) Clarkson, R. G. (to Du Pont Co.), *Ibid.*, 2,021,932 (Nov. 26, 1935).
(8) Collings, W. R., Peterson, F. C., and Kelly, H. C. (to Dow Chemical Co.), *Ibid.*, 2,235,798 (March 18, 1941).
(9) Downing, F. B., and Pedersen, C. J., (to Du Pont Co.), *Ibid.*, 2,121,397 (June 21, 1938).
(10) Dreyfus, H., *Ibid.*, 1,884,629 (Oct. 25, 1932).
(11) *Ibid.*, 2,007,950 (July 9, 1935).
(12) *Ibid.*, 2,015,104 (Sept. 24, 1935).
(13) *Ibid.*, 2,053,768 (Sept. 8, 1936).
(14) *Ibid.*, 2,098,335 (Nov. 9, 1937).
(15) *Ibid.*, 2,106,298 (Jan. 25, 1938).
(16) *Ibid.*, 2,186,101 (Jan. 9, 1940).
(17) *Ibid.*, 2,233,475 (March 4, 1941).
(18) Dreyfus, H., Dickie, W. A., and Sowter, P. F. C. (to Celanese Corp.), *Ibid.*, 1,950,664 (March 13, 1934).
(19) *Ibid.*, 1,978,785 (Oct. 30, 1934).
(20) Ellsworth, D. C. (to Du Pont Co.), *Ibid.*, 2,060,056 (Nov. 10, 1936).
(21) *Ibid.*, 2,123,883 (July 19, 1938).
(22) Ellsworth, D. C., and Haskins, J. F., *Ibid.*, 2,201,663 (May 21, 1940).
(23) Franke, H., *Deut. Färber-Ztg.*, 1932, 85–6; Gränacher, C., Brit. Patent 347,117 (April 17, 1929).
(24) Freeman, R. D. (to Dow Chemical Co.), U. S. Patent 2,348,677 (May 9, 1944).
(25) Freeman, R. D., Peterson, F. C., and Greminger, G. K., Jr., *Ibid.*, 2,308,692 (Jan. 19, 1943).
(26) Freeman, R. D., and Roberts, M. J., *Ibid.*, 2,331,858 (Oct. 12, 1943).
(27) Gloor, W. E. (to Hercules Powder Co.), *Ibid.*, 2,350,161 (May 30, 1944).
(28) Hanahan, M. L. (to Du Pont Co.), *Ibid.*, 2,231,467 (Feb. 11, 1941).
(29) *Ibid.*, 2,231,468 (Feb. 11, 1941).
(30) Henkel & Cie G.m.b.H., French Patent 808,699 (Feb. 12, 1937).
(31) Hercules Powder Co., "Sodium Carboxymethylcellulose", June, 1944.
(32) Hiatt, G. D. (to Eastman Kodak Co.), U. S. Patent 2,196,768 (April 9, 1940).
(33) Höppler, F., *Chem.-Ztg.*, 66, 132–5 (April, 1942).
(34) Houghton, A. A., and Craik, J. (to Imperial Chem. Ind.), U. S. Patent 2,253,297 (Aug. 19, 1941).
(35) Hunt, J. K., and Latham, G. H. (to Du Pont Co.), *Ibid.*, 2,086,419 (July 6, 1937).
(36) Hurd, I. S. (to Rohm & Haas Co.), *Ibid.*, 2,314,277 (March 16, 1943).
(37) I. G. Farbenindustrie A.-G., Brit. Patents 305,230 (Feb. 2, 1928) and 317,117 (May 9, 1928).
Ibid., 340,232 (Aug. 17, 1929).
Jacobson, I. M., and Truscott, S., U. S. Patent 1,706,295 (March 19, 1929).
(40) Jansen (to Deutsche Celluloid Fabrik Eilenburg), German Patent 332,203 (1918).
(41) Johnson, A. J. (to Du Pont Co.), U. S. Patent 1,979,869 (Nov. 6, 1934).
(42) Kallock, W. F. (to McLaurin-Jones Co.), *Ibid.*, 2,299,991 (Oct. 27, 1942).
(43) Kinnard, V., *Foreign Commerce Weekly*, May 15, 1943, pp. 11, 13.
(44) Köhler, R. (to Henkel & Cie G.m.b.H.), U. S. Patent 2,180,152 (May 14, 1939).
(45) Kojevnikoff, N. N. (to Du Pont Co.), *Ibid.*, 2,123,700 (July 12, 1938).
(46) Krestinskii, V., *Kunststoffe*, 23, 64 (1933); abstracted from *Novosti Tekhniki*, 15, No. 5, 5 (1933).
(47) Kropscott, E. L. (to Dow Chemical Co.), U. S. Patent 2,226,823 (Dec. 31, 1940).
(48) Larson, L. L. (to Du Pont Co.), *Ibid.*, 2,216,845 (Oct. 8, 1940).
(49) Lilienfeld, L., Brit. Patent 231,803 (April 4, 1924).
(50) Lilienfeld, L., U. S. Patent 1,682,293 (Aug. 28, 1928).
(51) *Ibid.*, 2,004,875 (June 11, 1935).
(52) Lilienfeld, L. (to Lilienfeld Patents Inc.), *Ibid.*, 2,176,085 (Oct. 17, 1939).
(53) *Ibid.*, 2,265,914 (Dec. 9, 1941).
(54) *Ibid.*, 2,265,915 (Dec. 9, 1941).
(55) *Ibid.*, 2,265,916 (Dec. 9, 1941).
(56) *Ibid.*, 2,265,918 (Dec. 9, 1941).
(57) *Ibid.*, 2,265,919 (Dec. 9, 1941).
(58) Maxwell, R. W. (to Du Pont Co.), *Ibid.*, 2,148,952 (Feb. 28, 1939).
(59) *Ibid.*, 2,162,460 (June 13, 1939).
(60) Maxwell, R. W., and Larson, L. L., *Ibid.*, 2,236,545 (April 1, 1944).
(61) Medl, R. C., Jr. (to Hercules Powder Co.), *Ibid.*, 2,340,072 (Jan. 25, 1944).
(62) *Ibid.*, 2,362,761 (Nov. 14, 1944).
(63) Meigs, F. M. (to Du Pont Co.), *Ibid.*, 2,170,828 (Aug. 29, 1939).
(64) *Ibid.*, 2,170,829 (Aug. 29, 1939).
(65) Merrill, W. J. (to Du Pont Co.), *Ibid.*, 2,184,312 (Dec 26, 1939).
(66) Metallgesellschaft A.-G., Brit. Patent 429,559 (May 31, 1935).
(67) Meyer, Georg, U. S. Patent 2,288,200 (June 20, 1942).
(68) Müller, P., and Herrmann, O. (to Du Pont Co.), *Ibid.*, 2,252,091 (Aug. 12, 1941).
(69) Natl. Paint, Varnish Lacquer Assoc., Sci. Sect., *Circ.* 688 (Aug. 1944).
(70) N. V. Philips Gloeilampenfabrieken (to Philips Lamps Ltd.), Brit. Patent 552,719 (April 21, 1943).
(71) Oxley, H. F., Thomas, E. B., and Downing, J. (to Celanese Corp.), U. S. Patent 2,184,564 (Dec. 26, 1939).
(72) Pense, W., and Bestian, H. (vested in Alien Property Custodian), *Ibid.*, 2,341,413 (Feb. 8, 1944).
(73) Peterson, N. R. (to Dow Chemical Co.), *Ibid.*, 2,336,636 (Dec. 14, 1943).
(74) Reichel, F. H. (to Sylvania Industrial Corp.), *Ibid.*, 2,267,217 (Dec. 23, 1941).
(75) Reichel, F. H., and Cornwell, R. T. K., *Ibid.*, 2,281,513 (April 28, 1942).
(76) Reichel, F. H., and Craver, A. E., *Ibid.*, 2,176,925 (Oct. 24, 1939).
(77) *Ibid.*, 2,245,499 (June 10, 1941).
(78) Roberts, M. J. (to Dow Chemical Co.), *Ibid.*, 2,331,859 (Oct. 12, 1943).
(79) Robie, N. P. (to Carborundum Co.), *Ibid.*, 2,280,852 (April 28, 1942).
(80) Schweitzer, Otto, *Rubber Chem. Tech.*, 13, 408–14 (1940); *Kautschuk*, 15, No. 10, 169–72 (1939).
(81) Sichel, Ferdinand, A.-G., Brit. Patent 496,354 (Nov. 29, 1938).
(82) Sponsel, K., *Melliand Textilber.*, 19, 738–9 (1938).
(83) Sullivan, R. W. (to Du Pont Co.), U. S. Patent 2,177,260 (Oct. 24, 1939).
(84) Thinius, K. (vested in Alien Property Custodian), *Ibid.*, 2,347,525 (April 25, 1944).
(85) Thomas, E. B., and Oxley, H. F. (to Celanese Corp. of America), *Ibid.*, 2,135,128 (Nov. 1, 1943).
(86) Underwood, W. F., and Rothrock, N. S. (to Du Pont Co.), *Ibid.*, 2,170,827 (Aug. 29, 1939).
(87) Voss, J. (to Kalle & Co. A.-G.), *Ibid.*, 2,179,457 (Nov. 7, 1939).
(88) Wallach, R. (to Sylvania Industrial Corp.), *Ibid.*, 2,273,677 (Feb. 17, 1942).
(89) *Ibid.*, 2,302,511 (Nov. 17, 1942).
(90) Wenck, P. R. (to Dow Chemical Co.), *Ibid.*, 2,358,549 (Sept. 19, 1944).
(91) Werle, E., *Chem.-Ztg.*, 65, 320 (1941).
(92) Woodhouse, J. C. (to Du Pont Co.), U. S. Patent 2,170,845 (Aug. 29, 1939).
(93) Wrede, H. (to Rudolph Koeppe & Co. Chemische Fabrik A.-G.), German Patent 714,870 (Nov. 12, 1941).
(94) Young, A. E., and Freeman, R. D. (to Dow Chemical Co.), U. S. Patent 2,308,664 (Jan. 19, 1943).

https://www.industrydocuments.ucsf.edu/docs/xjmx0000

79

Low Cost BL Binder Formulation-Use of Bentonite

Merritt

DATE

ISSUED TO

DATE LOANED

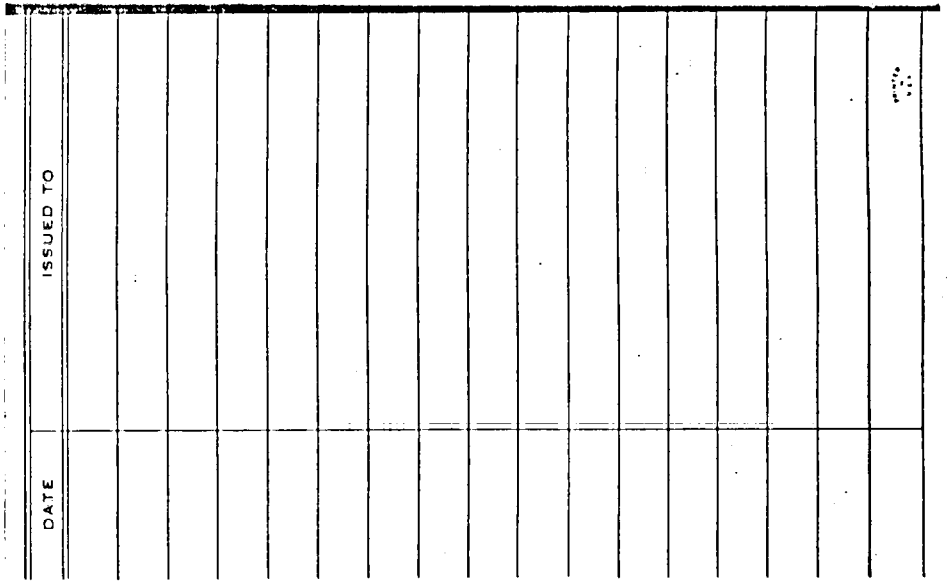
PRINTED IN U.S.A.

CAYLORD 3163

Ø000331103

Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000

0000331104



Source: https://www.industrydocuments.ucsf.edu/docs/xjmx0000